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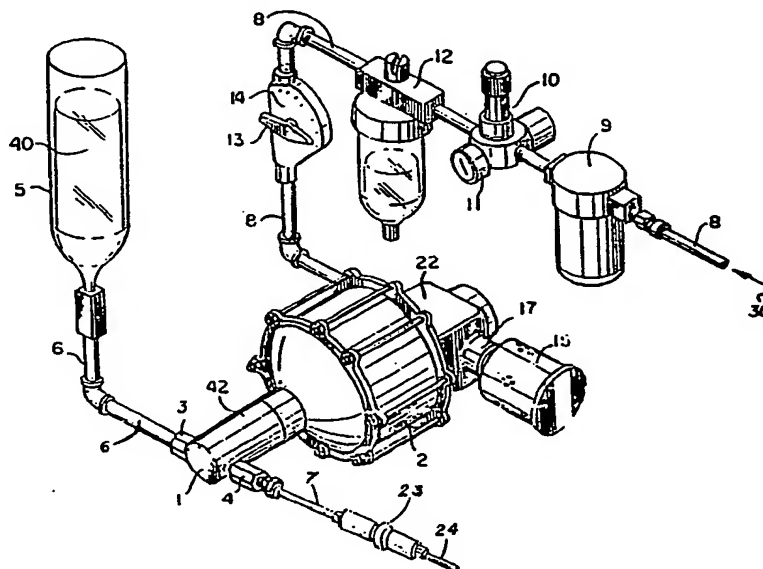




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## (54) Title: METHOD AND APPARATUS FOR THE MODIFICATION OF STARCH AND OTHER POLYMERS



## (57) Abstract

A method and apparatus for the modification of the physical properties of polymers through pressure processing techniques. The apparatus is comprised of a piston assembly (2) which acts on the polymer substrate charged within the confines of a compression chamber. Piston assembly (2) comprises compression chamber (1), the terminal end of which is disposed between inlet valve (3) and outlet valve (4), and piston housing (42) which has within it a movable piston (20). A reservoir (5) is provided as a receptacle for the substrate (40) and may be adapted with a stirrer and heating coils (not shown) where necessary to maintain homogeneity and flow properties. The piston delivers an abrupt pressure change to the substrate for the purpose of effecting the desired modification of physical properties including altered thermal, viscosity, solubility, turbidity and hardness profiles. Predictable characteristics may be imparted to the substrate through variation of pressure duration and intensity as well as the number of piston strokes applied. Modification of the physical properties of starch and gum arabic, in particular, is disclosed.

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## METHOD AND APPARATUS FOR THE MODIFICATION OF STARCH AND OTHER POLYMERS

### Technical Field

The subject invention relates to a method and apparatus for the physical modification of polymers in general, and to the production of novel starch compositions through the use of pressure processing techniques, in particular.

### Background Art

Starch, a natural polymer  $(C_6H_{10}O_5)_n$  derived from plant materials, is commonly found in the form of tiny microscopic granules (5-25 microns in diameter) comprised of stratified layers of starch molecules formed around a hilum nucleus. The starch granule shape may be round, oval or angular, and consists of a radially oriented crystalline aggregate of two anhydrous D-glucose polymers: amylose and amylopectin. The former is a straight chain polymer of several hundred glucose units linked by alpha-1-4-glycosidic linkages. Amylopectin is a branched polymer of several thousand glucose units with alpha-1-6-glycosidic linkages at the branched points and alpha-1-4 linkages in the linear regions. Individual branches may have between 20-30 glucose residues.

Heretofore, physical and chemical modification of starch has been accomplished through a variety of processes in order to realize improved performance characteristics in the food, paper, textile and pharmaceutical industries. For example, improved rheological and thermal stability properties of modified starches result in superior frozen, instant, dehydrated, and heat and serve food products which would not otherwise be economically competitive. Similarly, in the pharmaceutical industry, solubility and hardness properties of starch excipients are improved to effect the appearance and performance of tablets. Other physical properties of starches important to formulators and food processors today include viscosity, acid stability, moisture resistance or affinity, gel characteristics, decomposition rates (shelf life), shear

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1 affinity, gel characteristics, decomposition rates (shelf life), shear  
2 resistance, texture, mouth feel and clarity when in solution.

3 Modification of starch is conventionally accomplished through  
4 thermal or chemical means. Pregelatinization, for example, is the pre-  
5 cooking of starch and starch products to make them cold water soluble.  
6 This solubility property, more commonly referred to as "cold water  
7 swelling", finds utility in instant foods such as puddings, pie fillings,  
8 analogues, and textured products. Pre-cooking is accomplished by  
9 application of a starch slurry to a steam-heated roll where the starch is  
10 cooked instantly and dried. Thus, pregelatinized starches are those  
11 which have been hydrated and treated thermally. Through moisture and  
12 heat treatments the crystallinity of several starch products can be  
13 modified to provide desired property changes.

14 Starch may also be modified chemically by a process known as  
15 crosslinking to provide inhibition properties. Bi- or polyfunctional  
16 reagents such as phosphorus oxychloride are used to covalently bridge,  
17 or crosslink, two starch molecules at various locations along their chains  
18 to provide viscosity stability as well as acid, heat and shear tolerance.  
19 These properties find utility in acid foods (salad dressing and pie fillings),  
20 canned foods, gravies and sauces, cream-style corn, and oriental foods.

21 Another chemical modification process of starch is substitution.  
22 Here, the introduction of substituent groups on starch by treatment with  
23 monofunctional reagents which react with the hydroxyl groups on starch  
24 produces starch esters and starch ethers. Treating substituents include  
25 acetate, succinate, phosphate, hydroxypropyl, and octenylsuccinate.  
26 The primary purpose of substitution is to impart resistance to  
27 retrogradation and gelling of amylose and eliminate the association of the  
28 linear segments of amylopectin at low temperature. Other effects of this  
29 process include a lowering of gelatinization temperature, increased  
30 viscosity, improved colloidal properties, and modification of hydrophilic

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1 or hydrophobic character.

2 Still other chemical modification processes such as acid hydrolysis  
3 and oxidation may be employed to impart low hot paste viscosity, high  
4 alkali number, a high ratio of cold to hot paste viscosity, color changes,  
5 and high adhesive and binding powers to the starch composition.  
6 Starches so chemically modified find utility in the manufacture of gum  
7 candy and as coating agents for confections and breaded foods.

8 Each of the above modification processes, however, suffer from  
9 various shortcomings and result in starch products with physical  
10 property limitations. In the field of pharmaceuticals starch is frequently  
11 used as a binder for active ingredients and as a disintegrant upon  
12 contact with water or gastric solutions. Pregelatinized corn starch  
13 provides tablets with hardness properties in the range of 1 to 4 Kp.  
14 Present demands, however, require hardness levels in the range of 10 -  
15 14 Kp, an expectation which starch modified by prior art methods simply  
16 can not meet. While the use of starch in tableting formulations is still  
17 common practice, problems of uniformity between modified batches and  
18 a demand for tablets of greater hardness resulted in its departure from  
19 the status of a preferred pharmaceutical excipient.

20 Prior art methods of chemical starch modification are also  
21 inherently cost in-effective requiring the additional expense of  
22 crosslinking chemicals or functional reagents to produce the desired  
23 physical characteristics in the substrate. Disposal problems associated  
24 with unwanted reaction by-products further adds to cost and  
25 environmental concerns. Also, chemical modification methods yield  
26 product in batch quantities, rather than on a continuous or semi-  
27 continuous basis and, therefore, are less time efficient. Production rates  
28 are further diminished when more than one chemical modification must  
29 be made to the starch substrate to yield a product with all of the desired  
30 characteristics. Moreover, the starch end-product itself often suffers

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1 from other limitations similar to the deficient tablet hardness profiles,  
2 discussed above. Inferior viscosity, shear resistance and thermal profiles  
3 of the starch end-product, for example, may frustrate the performance of  
4 products incorporating starch modified by prior art means.

5 It is clear that a need exists for a method of modifying the  
6 physical properties of starch and other polymer compositions to provide  
7 improved performance characteristics useful in the food, pharmaceutical  
8 and other industries. The subject invention completely obviates all of  
9 the above described shortcomings by providing a method and apparatus  
10 for the physical modification of polymers such as starch by pressure  
11 processing techniques; the modified novel end-products themselves  
12 being characterized by improved physical properties.

13 Disclosure of the Invention

14 Applicant has discovered that the application of pressure to starch  
15 and other polymers as herein described results in the immediate  
16 conversion of the substrate to a form possessing modified physical  
17 properties.

18 A liquid substrate composition characterized as either a solution,  
19 slurry, dispersion, emulsion, mixture, suspension, or other substance  
20 exhibiting fluid dynamics, is treated by a piston apparatus wherein  
21 extreme heat and force are transmitted to the substrate resulting in its  
22 modification.

23 More particularly, the apparatus is comprised of a piston device  
24 which acts on the substrate charged within the confines of a  
25 compression chamber. The piston delivers a number of abrupt pressure  
26 changes to the substrate for the purpose of effecting the desired  
27 modification of physical properties. Specific predictable characteristics  
28 may be imparted to the substrate through variation of pressure duration  
29 and intensity as well as the number of piston strokes applied. It is  
30 theorized that the abrupt pressure changes also produce cavitation



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1 effects which aid in the modification process.

2 Accordingly, it is a primary object of the subject invention to  
3 provide a novel method and apparatus for affecting physical  
4 modifications in substrates.

5 It is another primary object of the subject invention to provide a  
6 method and apparatus for inducing changes in the physical properties of  
7 substrates.

8 It is also a primary object of the subject invention to provide a  
9 superior starch composition characterized by superior thermal, viscosity,  
10 solubility, turbidity and shear resistant properties.

11 Another object is to provide a method and apparatus for physically  
12 modifying a substrate and its physical properties through the application  
13 of one or more abrupt pressure changes to the substrate.

14 Another object is to provide a method for physically modifying a  
15 substrate and its physical properties through the application of at least  
16 one abrupt pressure change as produced by a piston apparatus.

17 An additional object is to provide a method and apparatus capable  
18 of modifying a substrate and its physical properties almost instantly  
19 upon exposure to one or more abrupt pressure changes.

20 Yet another object is to provide a cost effective and energy  
21 efficient method of physical modification of starch and other substrates  
22 without the necessity of chemical additives required by prior art  
23 processes.

24 Still another object is to provide a method for physically modifying  
25 a substrate and its physical properties which can be carried out on a  
26 semi-continuous basis.

27 With the above and such other objects in view as may hereafter  
28 more fully appear, the subject invention is comprised of the novel  
29 construction and combination of apparatus components, methods of  
30 their operation and resulting products as may be more fully appreciated

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1 upon reference to the accompanying drawings.

2 Description of the Drawings

3 Figure 1A is a Schematic diagram of the apparatus used to effect  
4 the modification of starch through abrupt pressure change treatments.

5 Figure 1B is a schematic diagram of the piston component of the  
6 pressure treatment apparatus used to effect the modification of starch  
7 through pressure shock treatments.

8 Figure 2A is a schematic diagram of the baffled chamber  
9 component of the pressure treatment apparatus.

10 Figure 2B is a cross section of the baffled chamber of Figure 2A  
11 taken along axis A-A.

12 Figure 3 compares various DSC spectra of a starch known as  
13 Capsul. Sample 1 is the DSC spectra this particular starch as it is  
14 supplied by the manufacturer in a raw untreated state. Sample 2 is a  
15 DSC spectra of Capsule starch after it has been treated by pressure at  
16 setting 60 for 5 recycle passes through the pressure treatment apparatus  
17 depicted in Figure 1. Sample 3 is a DSC spectra of Capsule starch after  
18 it has been treated by pressure at setting 90 for 5 recycle passes  
19 through the pressure treatment apparatus depicted in Figure 1.

20 Figure 4 shows the Thermographic analysis of various Capsul  
21 starches. Figure 4A Shows the TGA spectra of Capsul starch which has  
22 been dissolved into a solution and then dried in a vacuum oven into a dry  
23 powder.

24 Figure 4B shows the TGA spectra of Capsul starch which has  
25 been dissolved into a solution, pressure treated by the apparatus  
26 depicted in Figure 1 at setting 90 at just one treatment pass through  
27 the apparatus and then vacuum dried into a dry powder.

28 Figure 4C shows the TGA spectra of Capsul starch which has  
29 been dissolved into a solution, pressure treated by the apparatus  
30 depicted in Figure 1 at setting 90 for 20 re-cycle treatments and then

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1 vacuum dried into a dry powder.

2 Figure 5 is a DSC spectra of a starch known as Hylon 7 as  
3 supplied from the manufacturer, National Starch Co., in a raw untreated  
4 state.

5 Figure 5B is a DSC spectra of Hylon 7 starch after it has been  
6 treated by pressure in the device illustrated in Figure 1 at setting 90 for  
7 one pass.

8 Figure 6A is a solubility rate comparison of raw Capsul starch  
9 compared to two different forms of pressure treated starch, in ambient  
10 water. Figure 6B is a solubility rate comparison of raw Capsul starch  
11 compared to two different forms of pressure treated starch, in heated  
12 water. Figure 6C is a solubility rate comparison of raw Capsul starch  
13 compared to two different forms of pressure treated starch, in a warmed  
14 solution consisting of 1 N HCl and water, simulating human  
15 gastrointestinal fluids.

16 Figure 7 is a turbidity profile of raw capsule starch vs. two  
17 different forms of pressure treated Capsul starch.

18 Figure 8 is a viscosity profile indicating a comparison between raw  
19 capsul starch and pressure treated capsul starch.

20 Figure 9 is a Hardness profile of tablets made either Raw Capsul  
21 Starch, Pressure treated Capsul Starch or Microcrystalline cellulose.

22 Figure 10 is a dissolution profile of tablets made with 10%  
23 acetaminophen 90% starch, where the starch is either raw capsule  
24 starch or either of two pressure treated starch products.

25 Figure 11 is a illustration of the two basic components of starch,  
26 amylose and amylopectin, along with a table indicating the various types  
27 of starches available and their technical features.

28 **Detailed Description of the Invention**  
29 **And Best Mode For Carrying Out The Invention**

30 The discovery which is the subject of this invention is that the

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1 treatment of starch by piston strokes results in the modification of the  
2 substrate's physical properties. Reference is now made to Figure 1  
3 wherein a perspective view of the preferred embodiment of the subject  
4 apparatus is illustrated. The device as shown is comprised of a  
5 converted air-operated hydraulic pump with piston means for generating  
6 an abrupt pressure change to a target substrate 40 which is pumped  
7 through the apparatus.

8 A reservoir 5 is provided as a receptacle for the substrate 40 and  
9 may be adapted with a stirrer and heating coils (not shown) where  
10 necessary to maintain homogeneity and flow properties. Reservoir 5 is  
11 mounted to transfer conduit 6 which leads to pressure application  
12 assembly 2. Transfer conduit 6 may also be heated with heating coils to  
13 maintain the temperature of the substrate 40 as it passes to piston  
14 assembly 2. Piston assembly 2 comprises compression chamber 1, the  
15 terminal end of which is disposed between inlet valve 3 and outlet valve  
16 4, and piston housing 42 which has within it movable piston 20 (Figure  
17 2A). A series of seals and gaskets designated reference numerals 21  
18 and 50 are placed along compression chamber 1 to isolate the substrate  
19 40 from the balance of the piston assembly 2. Valves 3 and 4 may be  
20 solenoid, manually operated or automatic check valve devices. Movable  
21 piston 20 is displaced within housing 42 by motor 22 which may be  
22 hydraulic, pneumatic, electric or combustion powered. Output transfer  
23 conduit 7 is connected to exit valve 4 and leads to a separate baffled  
24 chamber 23 (Figure 2A).

25 Two modifications of the subject apparatus may be employed to  
26 regulate the closing of output valve 4. First, output transfer conduit 7  
27 may be of significantly lower inner diameter than input transfer conduit 6  
28 or compression chamber 1. This lower diameter acts to develop a back  
29 pressure within the system thereby causing output valve 4 to remain  
30 closed for a longer period. More particularly, Bernoulli principles are

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1 employed to interrupt the fluid flow at the point where the flow channel  
2 diameter decreases in size. While the velocity of fluid increases at this  
3 point, a back pressure is created which maintains spring loaded output  
4 check valve 4 in the closed position longer than would normally be  
5 experienced in a conventional hydraulic pump assembly. This function  
6 thus extends the pressure application period within compression  
7 chamber 1 which in turn facilitates physical modification to substrate 40  
8 and its properties.

9 Secondly, baffled chamber 23 (Figure 2A) comprises a housing 54  
10 within which a plurality of tabs or baffles 55 are provided for the  
11 purpose of inducing turbulence within the fluid and further adding to the  
12 back pressure effect discussed above. The length of chamber 23 may  
13 be varied to increase or decrease turbulence and back pressure to effect  
14 various physical property changes. Pressure treated substrate 40 enters  
15 the chamber 23 through inflow nozzle 57 which is contained within the  
16 inner diameter 56 of housing 54. Baffles 55 are actually a series of  
17 rings in the preferred embodiment as shown in the cross section (Figure  
18 2B). Baffles 55 protrude from the ring into the fluid flow causing  
19 turbulence and shear within the pressure treated substrate 40. It is  
20 theorized that the turbulence further promotes cavitation; an effect  
21 which will be discussed in greater detail below. It should be noted that  
22 other suitable means may also be employed to regulate the timing of  
23 valves 3 and 4 with departing from the intended purpose.

24 Compressed air 30 is delivered through an air conduit channel 8,  
25 an air filter 9, a regulator 10, an air flow oiler reservoir 12, a 1/4 turn air  
26 valve 14, and into an air motor 22. Air filter 9 is used to drain water  
27 from the compressed air supply 30. Regulator 10 controls the air  
28 pressure measured by pressure gauge 11. Minute oil droplets are  
29 introduced in the compressed air supply 30 as the air flows over a oil  
30 reservoir 12 to lubricate the air motor 22. Air motor 22 exhausts spent

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1 air through a muffler 15 which is connected to the outflow air port 17 of  
2 the air motor 22.

3 Air motor 22 cycles forward and backward as a result of the  
4 compressed air flow. The number of strokes of piston 20 (Figure 1B) is  
5 controlled by 1/4 turn air valve 14. A 90 degree incremental dial 13 is  
6 placed on valve 14. At setting zero, the valve is fully closed and no air  
7 flows to the air motor 22. At setting nine, which is 90 degrees to the  
8 horizontal, the valve is fully open and the full volume and force of the  
9 compressed air 30 is delivered to air motor 22. The 1/4 turn air valve  
10 14 is therefore the speed regulator of pressure applicator system 2,  
11 generally, and the stroke regulator of piston 20, specifically.

#### 12 OPERATION

13 The substrate 40 is charged to reservoir 5 in any state capable of  
14 flow through the system such as a pure liquid or carried by another liquid  
15 in the form of a mixture, solution, dispersion, suspension, emulsion,  
16 slurry or otherwise. Substrate 40 may be processed in heated, cooled or  
17 ambient temperature depending on its flow properties. While a wide  
18 variety of substrates 40 may be employed either alone or in combination  
19 with the method and apparatus of this invention, for purposes of  
20 disclosure it is convenient to consider and demonstrate them by their  
21 application to a natural polymer: starch.

22 Starch 40 is passed through the apparatus of Figures 1A and 1B  
23 and is pressure treated as the piston 20 strikes downward on its positive  
24 and negative displacement cycle within the pressure applicator housing  
25 2. Valves 3 and 4 may be locked in the closed position while piston 20  
26 is applying pressure to the starch 40 trapped between the valves in the  
27 compression chamber 1. Alternatively the valve action may be adjusted  
28 to provide a semi-continuous flow process. As piston 20 is raised  
29 through its negative pressure cycle within nose housing 42, a quantity of  
30 starch 40 is drawn past inlet valve 3 and into compression chamber 1

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1 where it is trapped when outlet valve 4 is in the closed position. As  
2 piston 20 is forced downward by air motor 22, it begins its pressure  
3 application or downward positive stroke cycle while both valves 3 and 4  
4 remain closed for a period of time sufficient to produce the desired  
5 pressure intensity within compression chamber 1. Spring loaded outlet  
6 valve 4 is adjusted to open when the desired pressure is reached  
7 permitting the treated starch 40 flow from the compression chamber 1  
8 through outlet transfer conduit 7 which may be heated and/or reduced in  
9 diameter for purposes described above. Baffle chamber 23 may similarly  
10 be employed, with or without the reduced diameter of conduit 7, to  
11 impart increased turbulence and back-pressure effects as earlier  
12 described. Substrate 40 finally exits the system through exit conduit 24  
13 for delivery into a collection vessel (not shown) for storage or  
14 subsequent drying. Alternatively, starch 40 may be recycled through the  
15 apparatus for exposure to additional pressure treatments or may be  
16 directed to one or more similar systems connected in series or parallel.

17 The resulting starch end-product manifests several changes in  
18 physical properties, including: an altered thermal profile (the onset of  
19 melting and the actual melting point is raised, the heat energy required  
20 to effect melting is also altered); altered disintegration and solubility  
21 properties (the solubility rate in water and other solutions in an ambient  
22 or heated environment is slowed by as much as 300%); an altered  
23 viscosity profile (pressure treated starch exhibits a higher viscosity for a  
24 longer period of time); an altered tableting profile (the treatment of waxy  
25 maize pre-gelatinized starches results in a starch which forms harder  
26 tablets at lower than conventional compression forces); and an altered  
27 turbidity profile (the clarity of solutions made with pressure treated  
28 starch is improved).

29 A feature of the subject apparatus believed to aid in these  
30 modifications of starch and its physical properties can be found within

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1 piston assembly 2. Reference is once again made to Figure 1B wherein  
2 one or more inserts or baffles 52 and 53 are placed within compression  
3 chamber 1 to retard fluid flow. These baffles 52 and 53 act to create  
4 turbulence within the compression chamber during pressure treatment  
5 and as starch 40 is pumped through piston assembly 2. Applicant  
6 theorizes that these baffles further act to generate cavitation within the  
7 compression chamber 1 as the piston 20 generates a abrupt pressure  
8 change.

9 The abrupt pressure change is believed to cause the liberation of  
10 gases trapped within the starch substrate 40, thereby generating heat.  
11 Various studies on cavitation show that the heat produced immediately  
12 upon cavitation can be very intense (5,000 degrees K or greater), even if  
13 only for a short period of time. The heat energy released is thought to  
14 be a major cause in the alteration of the physical properties of starch and  
15 other substrate compositions. Reference is made to the article, "The  
16 Temperature of Cavitation", by Flint and Suslick, American Association  
17 for the Advancement of Science, September 20, 1991, Volume 253, pp.  
18 1397-1398, wherein the heat energy caused by ordinary cavitation is  
19 discussed. Applicant theorizes that the heat energy released through  
20 cavitation is sufficient to cause a thermoreaction in the target substrate  
21 thereby contributing to its modification and that of its physical  
22 properties.

23 Moreover, applicant theorizes that the amylose and amylopectin  
24 components of the starch substrate 40 can be merged, compressed or  
25 deformed by the kinetic, compression and/or shear forces resulting from  
26 the abrupt pressure changes generated within the compression chamber  
27 1. Applicant, however, does not rule out as a possible mechanism the  
28 alternative possibility that it is the release of pressure forces, either  
29 during the pistons negative displacement or by the release of the  
30 pressurized starch through the check valve which contributes to property



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1 modification. It is possible that the chemical structure may be changed.  
2 Some substrates could be converted from an ionic to an anionic charge.  
3 Applicant has discovered the effect but does not know the mechanism.

4 A series of experiments were conducted to illustrate the effect of  
5 pressure treatments upon starch. In each case a device known as the  
6 Delta Processor, Model Number D-001 was employed. The device  
7 corresponded to the design illustrated in Figures 1A and 1B. The  
8 pressure applicator employed was a modified hydraulic pump supplied by  
9 S.C. Hydraulics Company, Model Number 10-600-8-ss-si. The tension  
10 on the output check valve was adjusted to open far slowly than would  
11 normally be the case for this model hydraulic pump. A calibration was  
12 made of the machines capabilities using distilled water to test the flow  
13 rate of the modified pump assemblage and the number of strokes per  
14 minute.

15 The apparatus employed in all of the following experiments was  
16 set at speed dial 4 and at either 60- or 90 psi on the regulator gauge.  
17 The pump system, however, multiplies the effective force of  
18 compression by 144x. The pressure applied in the compression chamber  
19 is effectively 8,640 lbs. at the 60 psi regulator position. At the 90 psi  
20 regulator position, the effective pressure in the compression chamber is  
21 12,960 lbs.

22 The timing of the opening of the output check valve controls how  
23 long the piston is in a downward or positive pressure position, i.e. how  
24 long the target substrate is under pressure. In the experiments described  
25 below, the machine was set for speed dial setting 4 at either 60 or 90  
26 psi. At the 60 psi setting, speed level 4, the transition time, the time by  
27 which the substrate was under direct positive compression was  
28 measured at 0.59 seconds. At the 90 psi setting, speed level 4, the  
29 transition time was measured at 0.53 seconds. The difference between  
30 the two pressure settings alters the transition time by only 0.06

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1 seconds, but the effective pressure differential was 4,320 psi.

2 **EXPERIMENT 1:**

3 300 grams of Capsul starch provided by National Starch Co., Inc.  
4 is mixed in 700 Mls distilled water at ambient temperature in a one liter  
5 beaker and stirred for 15 minutes until the Capsul starch is dissolved.  
6 The solution is then fed to the Delta Processor Unit Model No D-001,  
7 supplied by Encapsulation Systems Inc. The unit is set for either 60 or  
8 90 psi inlet pressure and the samples treated by a single pass through  
9 the apparatus. The effective pressure is multiplied 144 times to produce  
10 either 8,640 lbs. or 12,960 lbs. of pressure respectively. The treated  
11 starch is then delivered to a commercial spray drier device and dried to  
12 produce a dry powder product with less than 6% moisture.

13 Figures 3A-C depict DSC spectra of the resulting starch products.  
14 A differential scanning calorimeter device supplied by Dupont  
15 Instruments Corp. Model Number TA-2000 was employed.

16 Two comments are in order with respect to the DSC spectra  
17 presented below. First, the absolute height (or depth) of the peaks in  
18 the DSC spectra are reflective only of the mass of the sample used to  
19 generate that curve. Thus, differences in the height (or depth) of a peak  
20 from one spectra to another are not significant in terms of identifying  
21 potential changes in polymorphic structure or in the amylose to  
22 amylopectin ratio. The different polymorphic forms are distinguished by  
23 the fact that they melt at different temperatures. Secondly, all the DSC  
24 spectra have been presented at the same resolution and scale unless  
25 otherwise specifically noted.

26 The use of DSC spectra to characterize the physical structure  
27 changes in the target substrate was chosen to determine if any  
28 significant alterations in thermal profile or crystallinity structure had  
29 occurred as a result of this process. In many cases, the DSC spectra  
30 reveal a major shift in the thermal character of the substrate after

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1 treatment. This was clearly most evident on those compositions which  
2 exhibit a polymorphic crystalline structure such as starch.

3       Figures 3 are the DSC spectra of raw Capsul starch compared to  
4 Capsul starch pressure treated at both 90 and 60 psi. Graph 3A depicts  
5 the DSC spectra of raw Capsul Starch. Graph 3B shows Capsul starch  
6 which has been treated at the 60 psi setting. Graph 3C shows Capsul  
7 starch which has been pressure treated at the 90 psi setting. The  
8 significant difference relates to the starting point of melting of the starch  
9 products. The onset of melting begins at 78.28 (c) for the raw capsule  
10 starch. After pressure treating at the 60 psi setting for one pass the  
11 onset of melting is lowered to just 26.38 (c). After pressure treating at  
12 the 90 psi setting for one pass the onset of melting is lowered even  
13 further to 22.16 (c).

14       These DSC profiles clearly show that the thermal profile of starch  
15 may be altered through pressure processing.

16                                   **EXPERIMENT 2:**

17       300 grams of Capsul starch is mixed in 700 Mls distilled water at  
18 ambient temperature in a one liter beaker and stirred for 15 minutes until  
19 the capsul starch is dissolved. The solution is then fed to the Delta  
20 Processor Unit Model No D-001, supplied by Encapsulation Systems Inc.  
21 The unit is set for 90 psi inlet feed pressure. The effective pressure is  
22 multiplied 144 times to produce 12,960 lbs. of pressure upon the  
23 treated sample. The starch solution was subjected to either one pass  
24 through the process or twenty passes and compared with an untreated  
25 control solution.

26       The end-product was collected and, instead of spray drying, the  
27 solution was placed into a vacuum oven and dried at just 50 (C) under a  
28 vacuum until dried. The resulting product at this stage was crystalline in  
29 appearance and in the form of large agglomerates. These dried crystals  
30 were then ground in a ball mill grinder until a dry powder was obtained,

-16-

1 a final product with less than 2% moisture. This resultant product was  
2 then tested through a series of procedures to determine if it had  
3 characteristics different from the raw starch.

4       Figures 4A-C show the results of thermographic analysis of the  
5 Capsul starch which has been treated by the methods described in  
6 Experiment 2, with no pressure processing, as compared to two samples  
7 which were pressure treated. Figure 4A is the recovered control sample,  
8 with no pressure treatment. Note the start of thermal degradation  
9 begins at 61.72 (c). After one pass (Figure 4B) through the  
10 pressurization process the start of degradation jumps to 75.17 (C); a  
11 gain of 13.45 degrees. When treated for 20 passes (Figure 4C) the  
12 onset of degradation begins at 67.10 (C), still a gain over the control  
13 sample but far less than was achieved through the single pass sample.  
14 All of the pressurization samples were treated at the 90 psi setting.

15       Again the thermal profile is altered after pressure treatment. In  
16 the above example it can be seen that multiple pressure treatments can  
17 vary the thermal profile of a pressure treated starch, and that there are  
18 significant gains in thermal stability properties provided through pressure  
19 treatments.

#### 20                                   **EXPERIMENT 3:**

21       100 lbs of Hylon 7 starch is mixed in 25 gallons distilled water at  
22 ambient temperature in a 50 gallon stainless steel tank and stirred for 30  
23 minutes until the starch is dispersed. Hylon 7 is the name of high  
24 amylose starch supplied by National starch. It contains 70 % amylose  
25 and is often used as a gelling agent for jelly gum candies. Hylon 7 does  
26 not dissolve readily in water at room temperature.

27       The dispersion is then fed to the Delta Processor Unit Model No.  
28 D-001, supplied by Encapsulation Systems Inc. The unit is set for either  
29 60 or 90 psi inlet feed pressure.

30       The end product is then delivered to a tank where the excess

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1 water is eventually siphoned off, producing a wet cake product. The  
2 wet cake is then placed in a vacuum oven which is heated to 40° (C) to  
3 draw off the remaining moisture. A final dry product containing less  
4 than 5% moisture is produced which was then tested through a series of  
5 procedures to determine if it had characteristics distinguishable from the  
6 raw starch.

7 Figure 5A is the DSC spectra of Hylon 7 starch, supplied by  
8 National Starch Co., in raw form.

9 Figure 5B is the DSC spectra of Hylon 7 starch which has been  
10 pressure treated at the 90 psi setting. Note the extreme gain in the  
11 onset of melting between the two samples. The raw sample begins to  
12 melt at 68.75° (C) while the pressure treated sample does not begin to  
13 melt until 97.80° (C); a gain of 29.05 degrees. The melting in both  
14 samples is completed at nearly the same point, 113° (C), but more  
15 thermal energy is required to begin the melting of the pressure treated  
16 sample.

17 Figures 6A-C illustrate the dissolution profile for starch materials  
18 made according to the procedure described in experiment 1, whereby  
19 Figure 6A is a dissolution profile for raw Capsul starch vs. pressure  
20 treated starches processed at the 60 psi and 90 psi settings, in ambient  
21 water. Figure 6B depicts the same tests but in heated water and Figure  
22 6C depicts the results of the same tests in a 1N HCl solution, simulating  
23 human gastric fluid conditions. In each test, one gram of substrate was  
24 dissolved in 50 ml of the given solvent in a 150 ml flask subjected to a  
25 low setting shaker bath. Dissolution is the point at which the starch  
26 totally dissolves and the flask is clear according to either a visual  
27 observation or through the use of an ultraviolet spectrophotometer.

28 The time for complete dissolution is given along the "Y" axis in  
29 seconds. The "601" designation denotes that the sample was pressure  
30 treated at the 60 psi setting for 1 pass. Similarly, the "901" designation

-18-

1 denotes a 90 psi pressure setting for 1 pass.

2       The graphs of Figures 6A-C represent an average of 5 readings for  
3 each sample in each tested media and temperature condition. In each  
4 case the pressure treated capsule starch dissolves far slower than the  
5 untreated raw starch. There were unexpected differences between the  
6 601 and 901 products in differing media. For example, the 601 product  
7 has a slower dissolution in warm water than does the 901 product.  
8 Generally, however, the 901 product has a slower dissolution time in  
9 most media tested.

10       The graph depicted in Figure 7 shows the effect of pressure  
11 treatments on turbidity of the Capsul raw starch vs. the pressure treated  
12 samples made in experiment 1. Turbidity is the measure of transmitted  
13 light through a fluid. It is used to determine the cloudiness of liquids.  
14 The graph of Figure 7 shows a comparison of turbidity for the raw starch  
15 compared to the pressure treated starches, treated at setting 60 psi and  
16 90 psi.

17       A series of 1% solutions of the starch in distilled water were  
18 prepared and tested for their UV spectra using a Perkin-Elmer Lambda 38  
19 UV spectrophotometer. A reading was taken at various time intervals of  
20 the percent light penetration operating at 600 nm wavelengths of  
21 ultraviolet transmission. From the graph it can be seen that the greatest  
22 light penetration and hence, the clearest solution, is exhibited by the  
23 pressure treated starch samples, with the greatest clarity profile  
24 exhibited by the sample treated at 90 psi.

25       Figure 8 provides a comparison of the relative viscosity profiles of  
26 raw Capsul starch and pressure treated starch processed at the 90 psi  
27 setting from Experiment 1. Figure 8 reveals four plots representative of  
28 two different batch runs through a Rapid Visco-Analyzer, model no.  
29 RVA3D, from Foss Food Technologies Inc. Viscosity profiles often  
30 indicate pasting characteristics for the starch. RVU = Relative Viscosity

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1 Units. The samples are heated over time and the viscosity is  
2 automatically measured and plotted.

3 Raw starch #1 and Raw starch #3, are from two different batches  
4 of raw Capsul starch as supplied by the manufacturer. Delta Starch 901  
5 (#2) and Delta starch 901 (#4) are two different samples of the pressure  
6 treated Capsul starch processed at 90 psi for one pass.

7 Examination of the graphs reveal that raw Capsul starch has a  
8 very short period during which it exhibits a high viscosity, and quickly  
9 loses that viscosity character over time. An examination of both raw  
10 starch visco-graphs indicates that there is poor uniformity within the raw  
11 starch batches.

12 The pressure treated samples, however, exhibit a greater  
13 uniformity between samples and also provide a higher viscosity profile  
14 for a longer period of time in comparison to the untreated samples. This  
15 result means that less heat energy is needed to achieve the desired  
16 viscosity profile; less heat, for a shorter period of time, passing on  
17 energy savings to the manufacturer. The use of emulsifiers and other  
18 thickeners may also be avoided through the use of the pressure treated  
19 starch products in certain food applications, because the pressure  
20 treated starch affords a superior viscosity profile.

21 Treated starch samples were also tested as excipients in tableting  
22 processes to determine their respective hardness profiles. The need for  
23 a more readily dissolvable diluent than microcrystalline cellulose was  
24 identified in various pharmaceutical surveys of tableters. To test the  
25 effectiveness of pressure treated starch, initial tests were carried out by  
26 forming tablets composed of 100% starch vs. 100% microcrystalline  
27 cellulose. Figure 9 reveals the hardness profile of the resulting  
28 pharmaceutical tablets.

29 Each tablet was composed solely of 200 mg. of the indicated  
30 material. No other binders or lubricants were employed. Raw Capsul

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1 starch was used as a base for comparison purposes along with Avicel  
2 Ph-101, a microcrystalline cellulose product supplied by FMC  
3 corporation. Standard tablets were made using a direct compression  
4 process in a Carver laboratory single stroke tablet press machine. The  
5 tablets were then tested using a conventional stokes tablet hardness  
6 tester device. The profile given in the graph of Figure 9 reveals that the  
7 greatest hardness is exhibited by the pressure treated starch treated at  
8 90 psi. Microcrystalline cellulose affords a high hardness and the  
9 pressure treated starch exhibits a high hardness as well but softer than  
10 the tablets made with either the 90 psi sample or the microcrystalline  
11 cellulose, while the raw starch affords a very soft tablet. In fact, the raw  
12 starch tablet was highly friable and broke readily in the hand.

13 The hardness profile reveals that the 90 psi sample provides the  
14 greatest hardness while requiring the lowest overall pressure treatment  
15 from the tableting press. Accordingly, starch treated at 90 psi may  
16 serve as an effective excipient for those active drug agents which are  
17 sensitive to the friction developed during tableting at high pressure  
18 tonnage and, therefore, difficult to tablet. The lower hardness profiles of  
19 the 60 psi end-products find utility as excipients in chewable tablet  
20 formations.

21 Next, tablets were made using 10% acetaminophen and tested for  
22 a dissolution profile. Figure 10 depicts the results of a comparison  
23 between raw Capsul starch and three different samples pressure treated  
24 at 60 psi/1 pass; 90 psi/1 pass and 90 psi/5 passes. The graph  
25 illustrates that the fastest dissolution time occurred for the raw  
26 starch/acetaminophen tablet. The lowest dissolution profile occurred  
27 with the 90 psi/1 pass treated starch; the other two samples possess  
28 altered dissolution profiles.

29 Additional tableting studies were conducted using Vitamin C and  
30 Acetaminophen active agents. Table I, below, indicates the composition



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1 formulated tablets. Note the extreme hardness provided by the pressure  
2 treated starch sample which is identified as "Delta starch" as compared  
3 to microcrystalline cellulose (Avicel 101). The particular starch used  
4 was pressure treated at 90 psi/1 pass according to the method  
5 Experiment 1. Also note that the treated starch tablets exhibit a superior  
6 appearance with no chipping defects.

TABLE I

## Tablet Formulations

9 <u>FAA0309</u>		10 <u>FAA0309A</u>	
11 Ascorbic Acid	255 mg	Ascorbic Acid	255 mg
12 Avicel 101	159 mg	D-Starch	159 mg
13 Stearic Acid	12 mg	Stearic Acid	12 mg
14 Aerosil 200	2 mg	Aerosil 200	2 mg
<hr/>		<hr/>	
15 Tablet Weight	428 mg	Tablet Weight	428 mg
16 <u>FAP0309A</u>		17 <u>FAP0309B</u>	
18 Acetaminophen	150 mg	Acetaminophen	150 mg
19 Avicel 101	264 mg	D-Starch	264 mg
20 Stearic Acid	12 mg	Stearic Acid	12 mg
21 Aerosil 200	2 mg	Aerosil 200	2 mg
<hr/>		<hr/>	
22 Tablet Weight	428 mg	Tablet Weight	428 mg

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TABLE II

## Physical Properties of Tablets

<u>Formula</u>	<u>Weight</u> <u>***</u>	<u>Thickness**</u>	<u>Hardness</u>	<u>Friability</u>	<u>Disintegration**</u>
FAAO309	440 mg	0.251"	9.14 SC	-0.45%*	Less than 60 Seconds
FAAO309 A	420 mg	0.257"	20.60 SC	-0.72%	9 Minutes
FAP0309 A	431 mg	0.250"	13.76 SC	-2.21%*	Less than 60 Seconds
FAP0309 B	436 mg	0.291"	36.77 SC	-0.00%	50% Weight Loss at 10 Minutes

- \* Corner chipping observed  
 \*\* Average of three readings  
 \*\*\* Average of ten tablets

Tablets were then tested for disintegration properties. In each of the microcrystalline cellulose tablets, disintegration occurred in less than 60 seconds. The pressure treated starch tablets, on the other hand, required 9 to 10 minutes indicating a much slower release profile. In the case of acetaminophen, which is used often as headache remedy, faster release is desired. This may be accomplished by adding disintegration enhancers to the tablet formula such as, for example, sodium bicarbonate.

Table III, below, shows the hardness of vitamin C (ascorbic acid) tablets made using microcrystalline cellulose and pressure treated "Delta" starch, respectively. Again, the starch used was treated at 90 psi/1 pass and the formulations used for the tablet corresponded to those depicted in Table II, above. As predicted, hardness profiles similar to those described above were realized.

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TABLE III

**Compressibility Profiles of Ascorbic Acid Tablets  
Prepared with D-Starch and Avicel 101**

<u>Formula #</u>	<u>Pressure</u>	<u>Hardness</u>	<u>Appearance</u>
FAA0309	Low	3.95 SC	Smooth Surface, Slightly Shiny
	Optimum	9.14 SC	Smooth Surface, Shiny
	High	19.60 SC	Smooth Surface, Shiny
FAA0309A	Low	0.00 SC	Rough Surface, Dull
	Optimum	5.04 SC	Rough Surface, Dull
	High	21.63 SC	Smooth Surface, Slightly Shiny
	Optimum/High	20.59 SC	Smooth Surface, Slightly Shiny

**EXAMPLE 4**

Acacia gum, also known as gum arabic, was treated according to the same methods employed on starch as described in Example 1. The acacia gum was purchased from TIC Gums, Inc.

Figures 11A-C are the DSC spectra of the various samples of gum arabic treated. Figure 11A results from the raw gum arabic as received from the supplier. Figure 11B results from gum arabic treated at 60 psi/5 passes. Figure 11C results from gum arabic treated at 90 psi/5 passes.

Referring to Figure 11A it can be seen that an endothermy exists at 61.75° C for the raw untreated gum arabic. Figure 11B reveals an endothermy increase to 95.91° C, a difference of 34.16° C. This figure represents the gain in the temperature starting point for decomposition. Figure 11C reveals an increase in the starting point of decomposition depicted at 104.74° C.

A comparison of the decomposition starting points for all three

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1 gum arabic samples shows that the 60 psi/5 pass pressure treated  
2 sample had a gain of 34.16° C whereas the 90 psi/5 pass sample had a  
3 gain over the 60 psi/5 pass sample of 8.8° C and a very significant gain  
4 of 42.99° C over the control sample. The 90 psi/5 pass sample thus  
5 realized a thermal stability modification enabling it to withstand 58.95%  
6 more thermal energy before the onset of decomposition than can the  
7 untreated acacia.

8 A dissolution study was also performed the results of which are  
9 illustrated in the graphs of Figures 12, 13 and 14. Referring to Figure  
10 12 it can be observed that both pressure treated samples exhibited  
11 slower dissolution rates in ambient distilled water than did untreated  
12 sample. There was little difference between the averaged 60 psi and 90  
13 psi samples. Figure 13 reveals a greater difference between the two  
14 pressure settings, when subjected to 100° F distilled water. In both  
15 cases the pressure treated samples dissolved at a slower rate compared  
16 to the raw sample. Finally, Figure 14 reveals the dissolution profile of all  
17 samples in 1 Normal HCL solution at 100° F. Again, the pressure  
18 treated samples exhibit slower dissolution rates compared with the  
19 untreated samples.

20 The following table summarizes the general results observed for  
21 the Gum Arabic samples:

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**TABLE IV**  
**Gum Arabic Comparisons**

Average	Dissolution Times*			Note
	Sample #5	Sample #6	Sample #7	
	60 psi	90 psi	Raw Control	
Average of 5 Runs				
	18:51	18:49	15:40	Room Temp. H <sub>2</sub> O
Average of 5 Runs				
	17:41	21:52	14:01	100° F H <sub>2</sub> O
Average of 5 Runs				
	27:56	28:51	14:38	1N HCL 100° F

\* Dissolution time given for sample to totally dissolve in minutes and seconds.

From the above examples and associated experimental results it can be appreciated that other physical properties of starches and acacia gum may also be modified via the subject pressure processing techniques. Additionally, it should be further appreciated that the subject method and apparatus may be employed to impart modified physical properties unto other substrate compositions or combinations thereof, as well.

Thus, it should be understood that the examples described herein are merely illustrative and not intended to limit the invention's ability to modify the structure and physical properties of other polymers such as those referenced in the following tables.

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**TABLE V****Partial List of Starches**

Potato  
 Tapioca  
 Corn  
 Waxy Maize  
 Wheat  
 Rice  
 Amycomaize  
 Pre-Gelatinize Starches  
 Starches of Varying Amylose and Amylopectin Ratios  
 Modified Starches  
 Genetically Engineered Starches

**TABLE VI****Partial List of Natural Polymers**

16	Carboxymethylcellulose	Cellulose Acetate Phthalate
17	Ethylcellulose	Gelatin
18	Gum Arabic	Starch
19	Bark	Methylcellulose
20	Arabinogelactan	Zein
21	Nitrocellulose	Propylhydroxylcellulose
22	Shellac	Succinylated Gelatin
23	Waxes, Paraffin	Proteins
24	Kraft Lignin	Natural Rubber
25	All other natural polymers listed in: "Polymer Handbook", Second	
26	Edition, Editors: Brandrup, Immergut	

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## TABLE VII

## Partial List of Synthetic Polymers

1		
2		
3	Polyvinyl Alcohol	Polyethylene
4	Polypropylene	Polystyrene
5	Polyacrylamide	Polyether
6	Polester	Polyamide
7	Polyurea	Polyvinyl Acetate
8	Ethylene Vinyl Acetate Copolymer	Epoxy
9	Polyvinylidene Chloride	Polyvinyl Chloride
10	Polyacrylate	Polyacrylonitrile
11	Chlorinated Polyethylene	Acetal Copolymer
12	Polyurethane	Polyvinylpyrrolidone
13	Poly (P-Xylene)	Polymethyl Methacrylate
14	Polyhydroxyethyl Methacrylate	
15	All other synthetic polymers listed in: "Polymer Handbook", Second	
16	Edition, Editors: Brandrup, Immergut	

17        Although the present invention has been described with reference  
18 to the particular embodiments herein set forth, it is understood that the  
19 present disclosure has been made only by way of example and that  
20 numerous changes in details of construction may be resorted to without  
21 departing from the spirit and scope of the invention. Thus, the scope of  
22 the invention should not be limited by the foregoing specifications, but  
23 rather only by the scope of the claims appended hereto.

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**1 WHAT IS CLAIMED IS:**

- 2 1. A method for modifying the physical properties of a polymer  
3 substrate, comprising:
  - 4 a. charging the polymer to a chamber wherein it may be  
5 subjected to an abrupt pressure change; and
  - 6 b. subjecting the polymer to an abrupt pressure change  
7 through a liquid media.
- 8 2. The method of claim 1, wherein said polymer is starch.
- 9 3. The method of claim 1, wherein said polymer is gum arabic.
- 10 4. An apparatus for modifying the physical properties of a polymer  
11 substrate, comprising:
  - 12 a. a chamber through which the polymer is passed;
  - 13 b. an inlet valve attached to said chamber;
  - 14 c. an outlet valve attached to said chamber;
  - 15 d. a piston housing attached to said chamber;
  - 16 e. a movable piston positioned within said housing so that the  
17 piston may act upon the polymer; and
  - 18 f. a means for moving the piston wherein the polymer  
19 substrate held within the chamber by the closure of the  
20 valves is subjected to the compression/expansion cycles of  
21 the piston when the piston is displaced.
- 22 5. The apparatus of claim 4 wherein at least one insert is placed  
23 within said chamber for the purpose of promoting physical modification  
24 of the polymer substrate during said compression/expansion cycles of  
25 the piston.
- 26 6. The apparatus of claim 4 wherein means for regulating the  
27 duration of said compression cycle is provided for the purpose of  
28 promoting physical modification of the polymer substrate.
- 29 7. The apparatus of claim 6 wherein said means for regulating the  
30 duration of said compression cycle is a baffle chamber; said baffle



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1 chamber being employed to create back-pressure on said outlet valve  
2 and within said chamber.

3 8. A polymer having modified physical characteristics treated in  
4 accordance with the method of claim 1.

5 9. The polymer of claim 8 wherein said polymer is starch.

6 10. The polymer of claim 8 wherein said polymer is gum arabic.

7 11. A starch composition characterized by at least one of the  
8 following physical properties: altered melting point, decreased solubility  
9 rate.

10 12. The starch composition of claim 11 further possessing one or  
11 more of the following characteristics: increased clarity, increased  
12 viscosity, increased thermal stability, increased resistance to shear  
13 forces, ability to form tablets of superior hardness.

14 13. A gum arabic composition characterized by at least one of the  
15 following physical properties: decreased solubility rates, increased  
16 thermal stability.

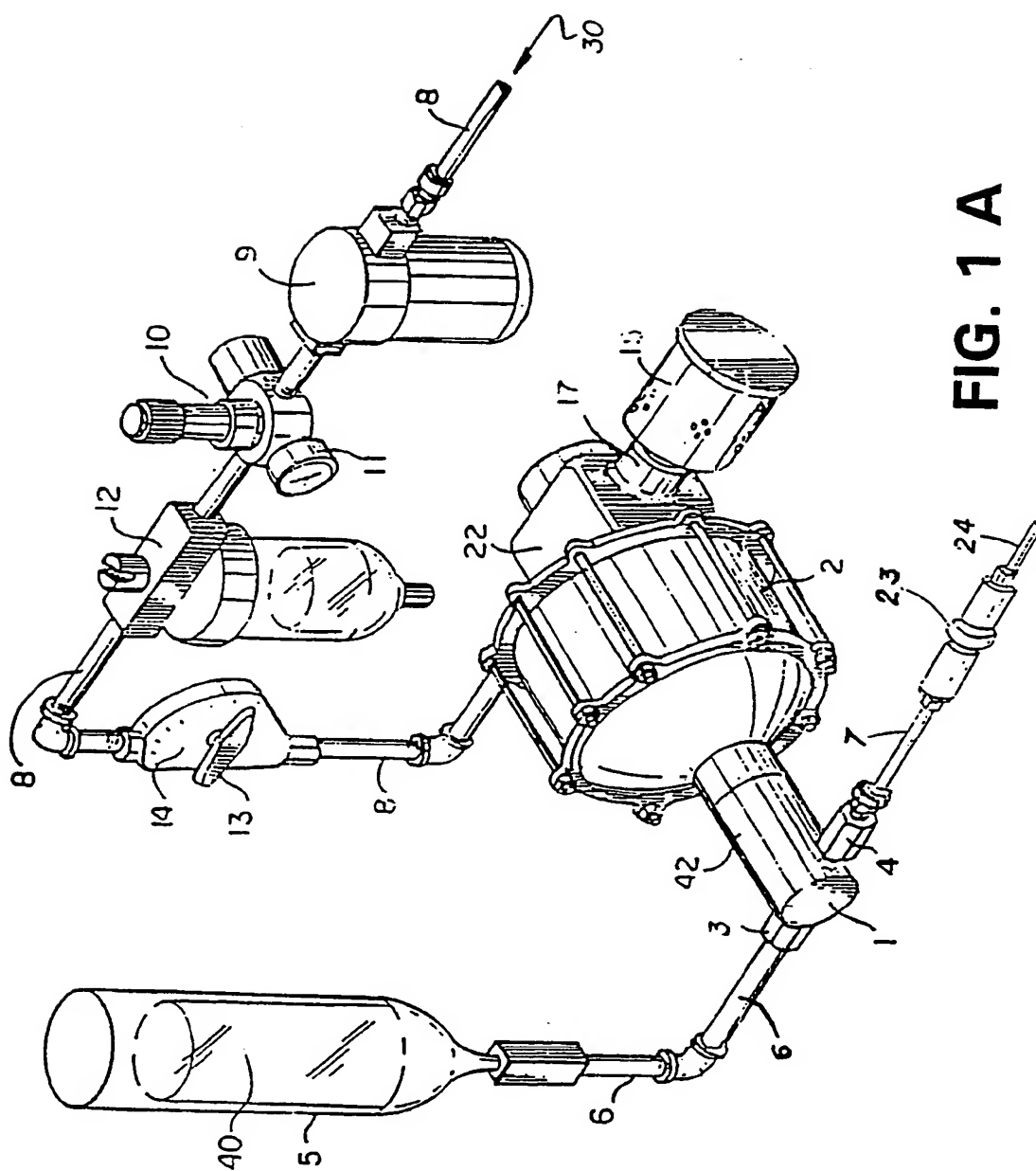


FIG. 1 A

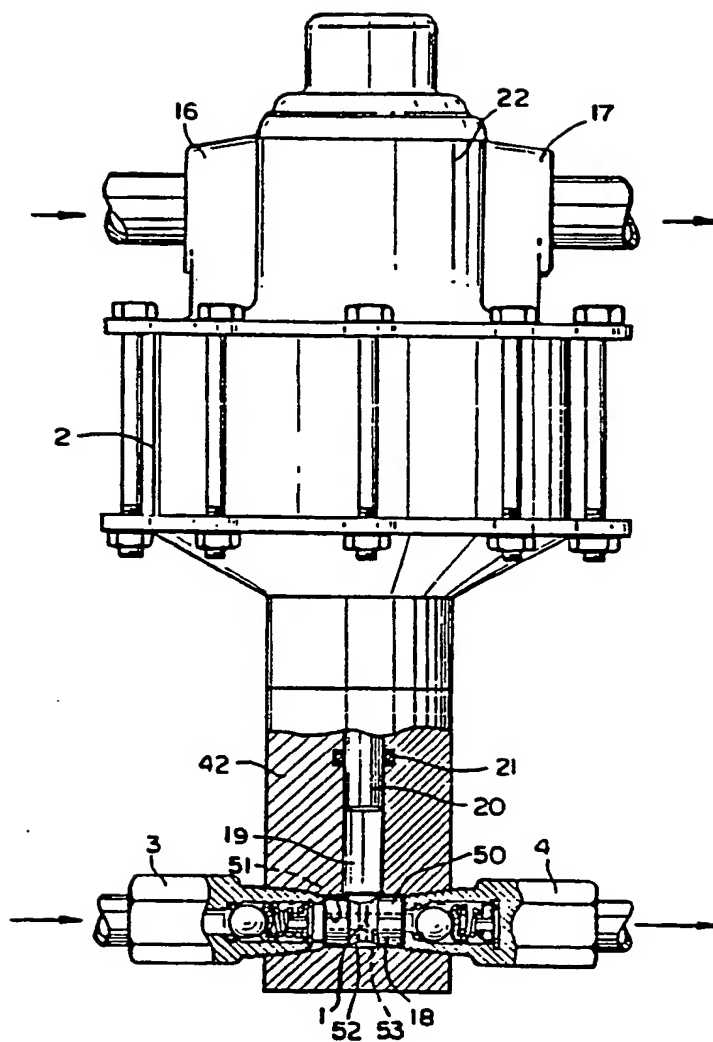


FIG. 1 B

FIG. 2 A

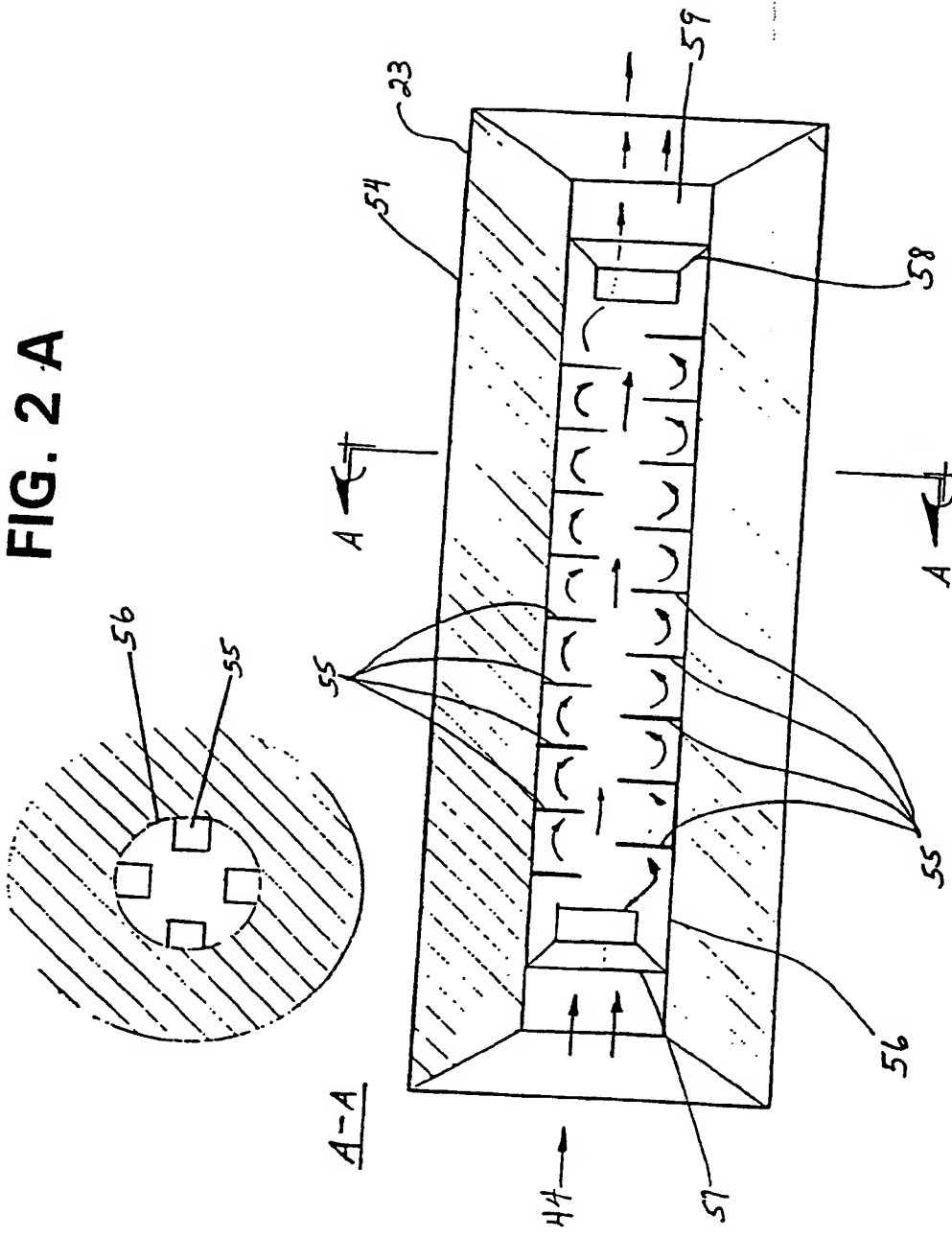
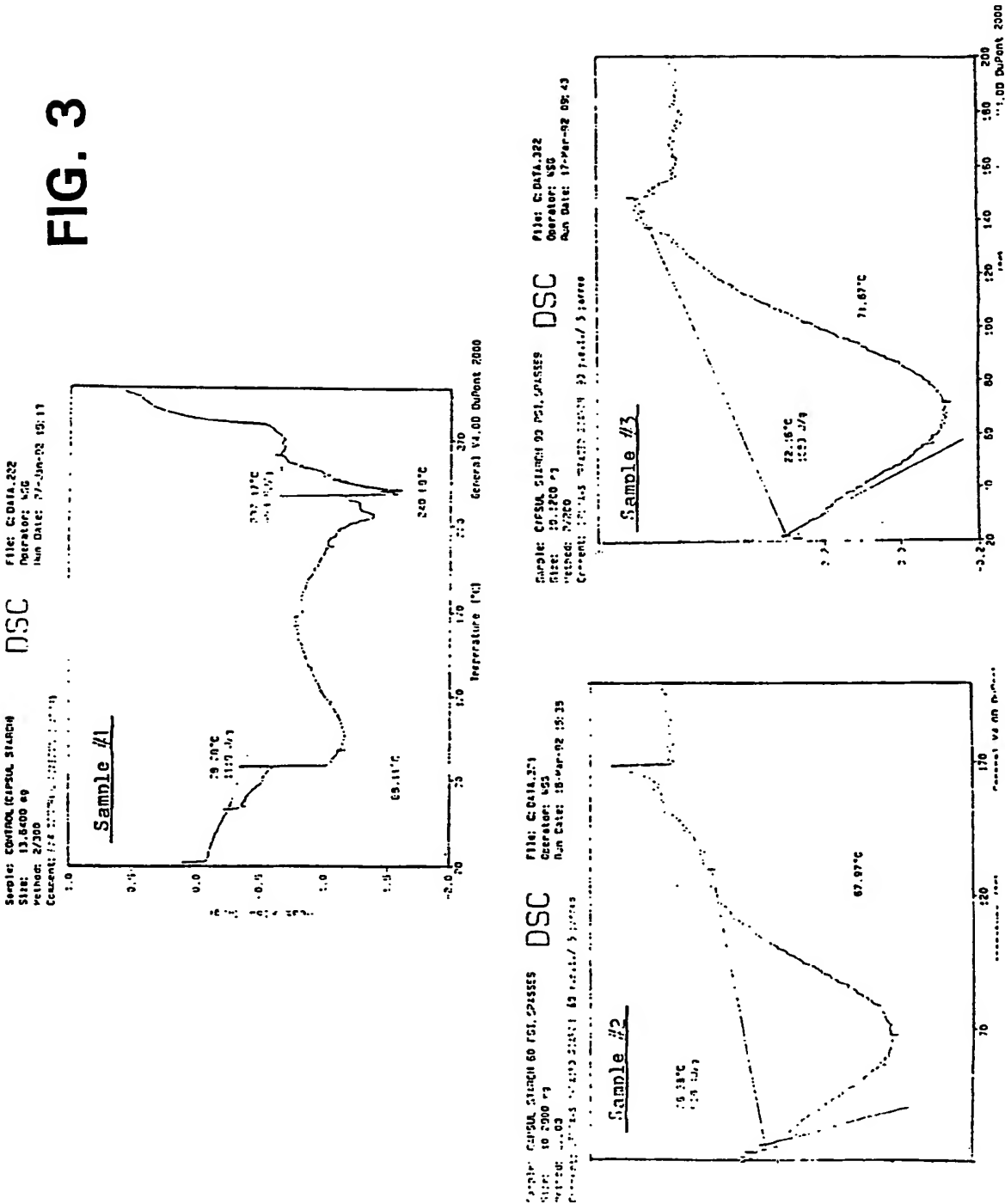
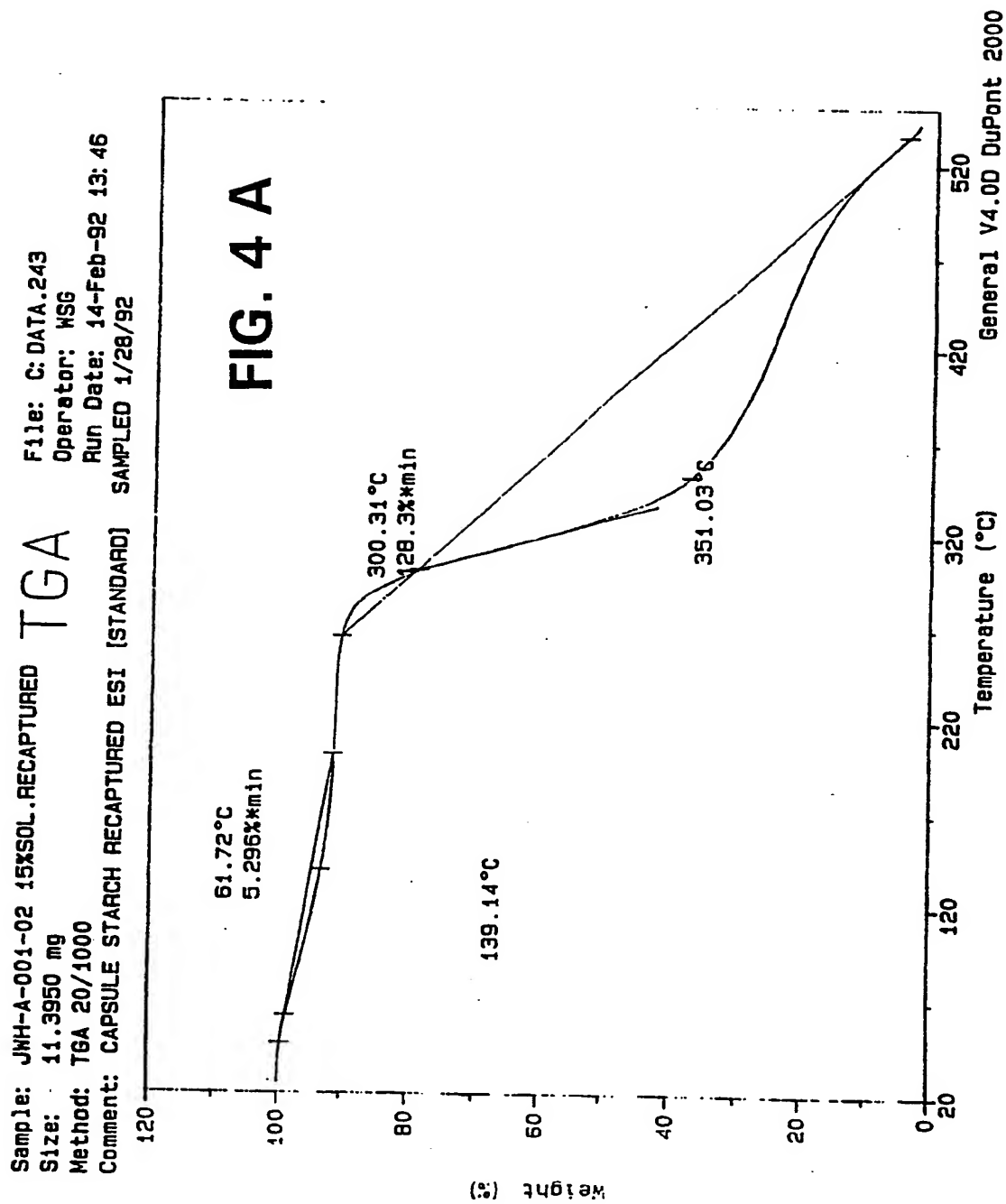


FIG. 2 B

FIG. 3

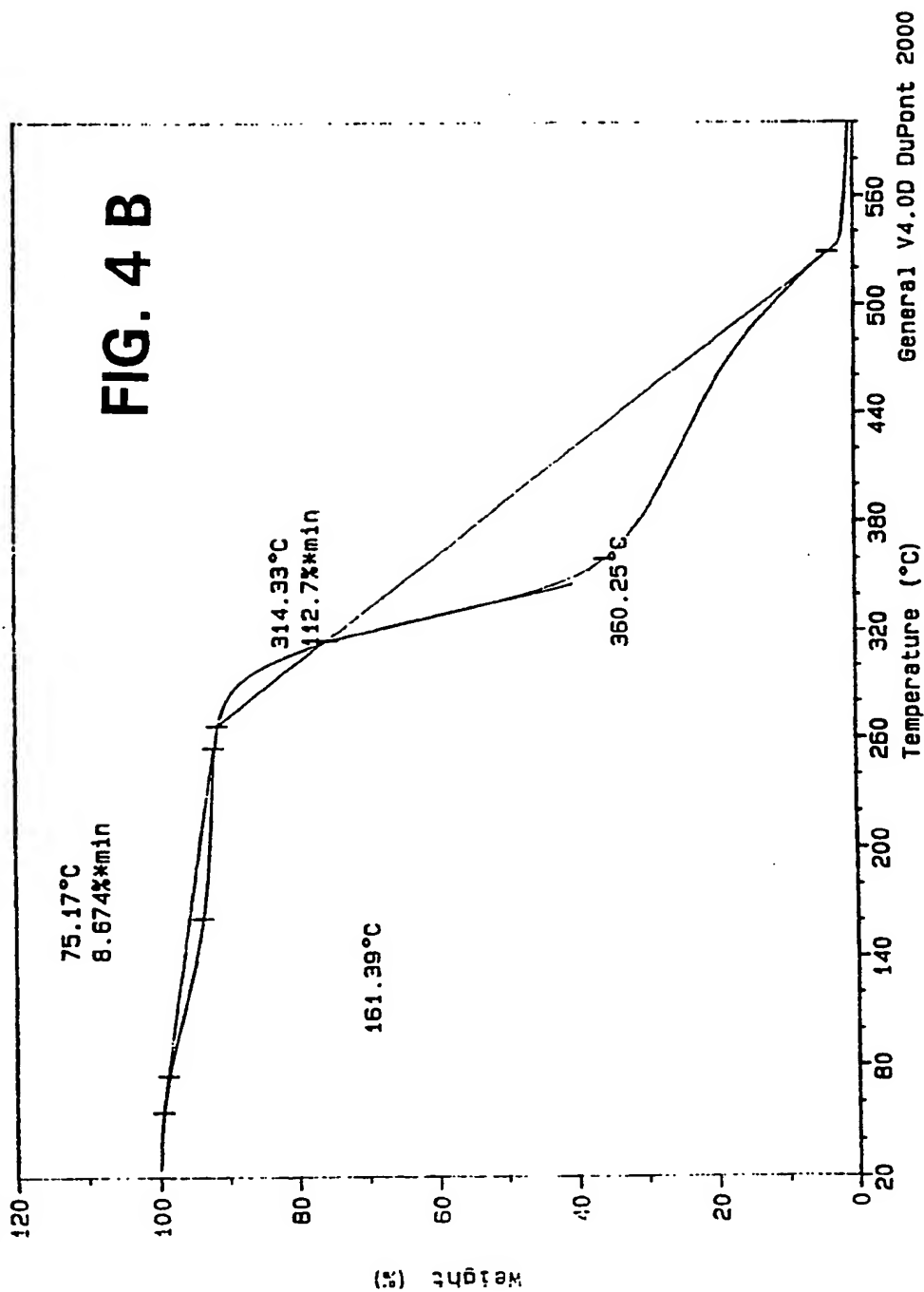


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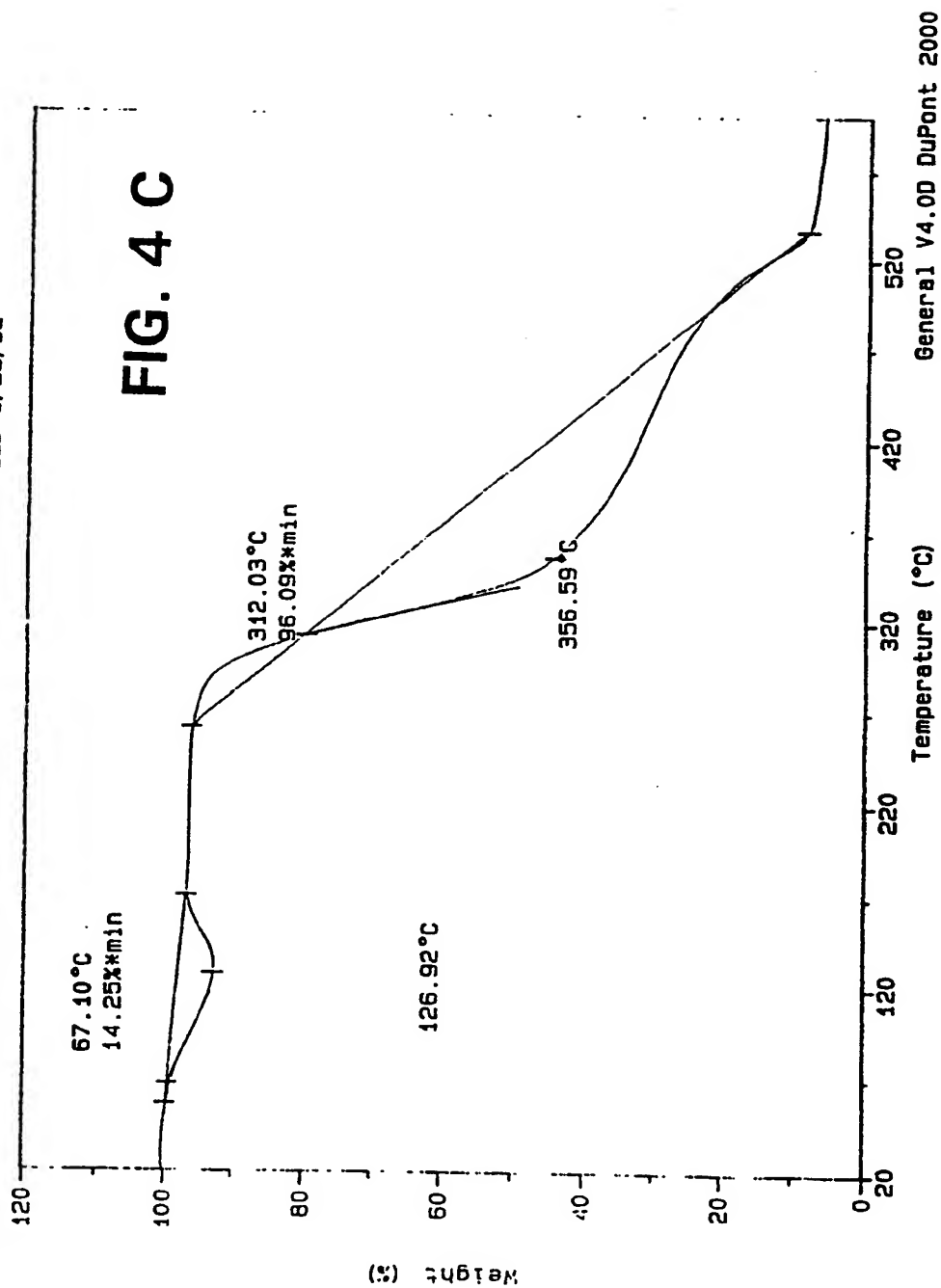
6/19

Sample: JWH-A-001-02 15%SDL.90PSI 1PASS TGA File: C:DATA.242  
Size: 9.9680 mg Operator: WSG  
Method: TGA 20/1000 Run Date: 14-Feb-92 11:26  
Comment: CAPSULE STARCH RECAPTURED ESI SAMPLED 1/28/92



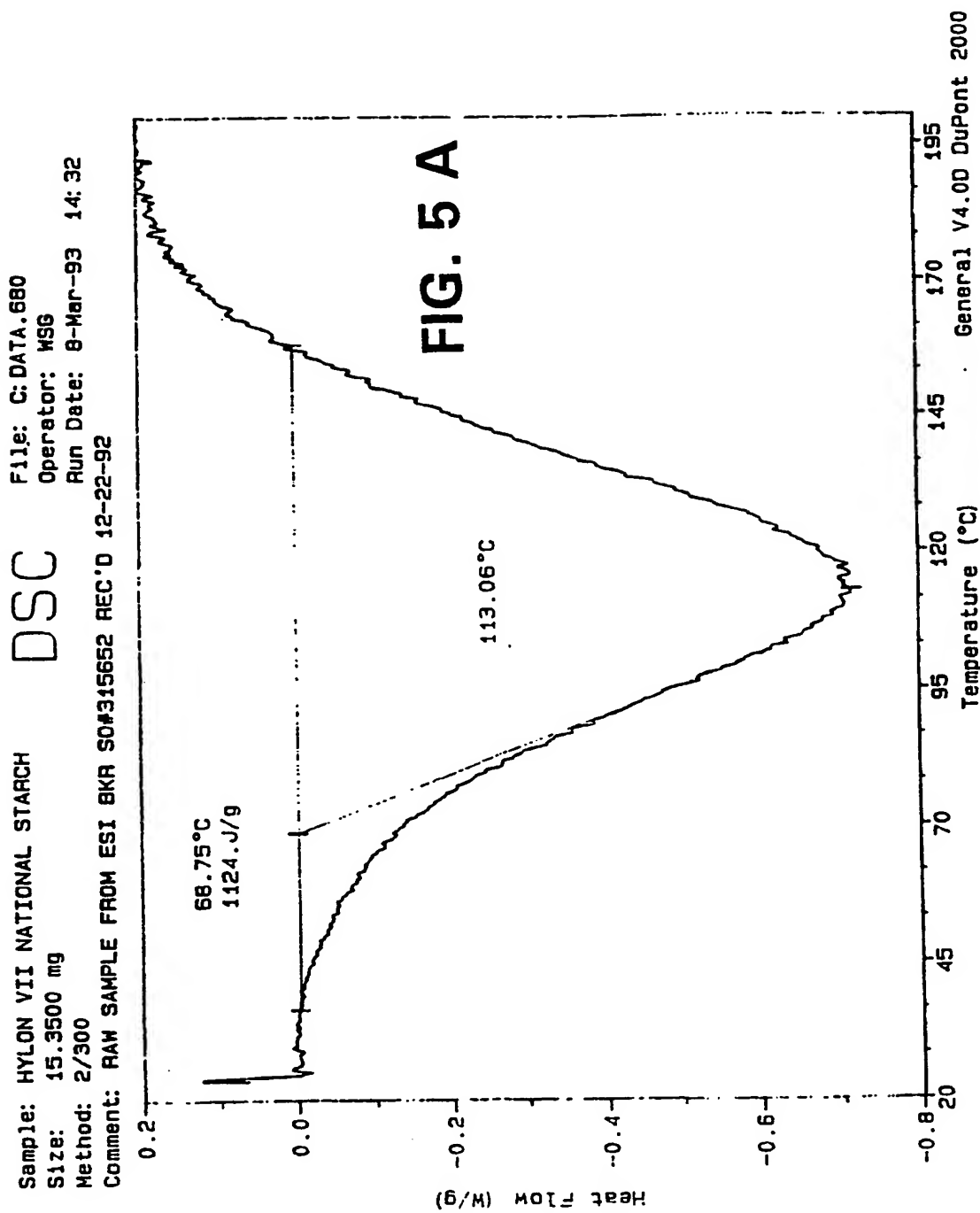
7/19

Sample: JWH-A-001-02 15% SOL. 90PSI 20PASS TGA  
Size: 10.7930 mg  
Method: TGA 20/1000  
Comment: CAPSULE STARCH RECAPTURED ESI  
File: C: DATA.241  
Operator: WSG  
Run Date: 14-Feb-92 09:05  
SAMPLED 1/28/92





8/19

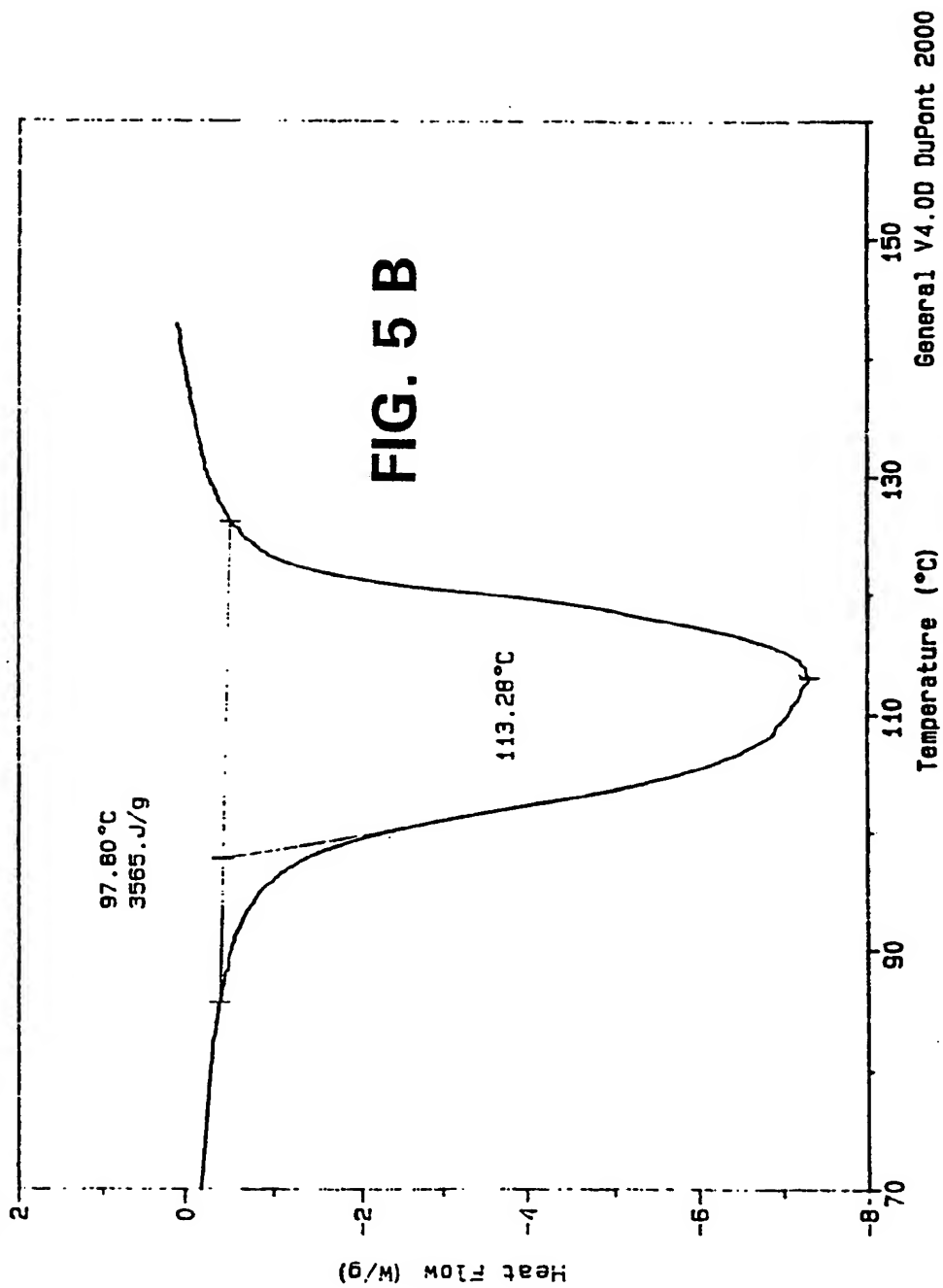


9/19

Sample: HYLON VII NATIONAL STARCH DELTA  
Size: 11.6000 mg  
Method: 2/300  
Comment: DELTA SAMP.FROM ESI BKR SO#315652 REC'D 3-4-93

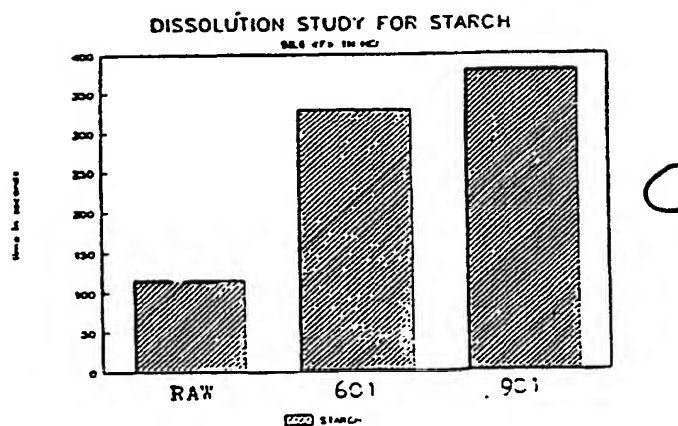
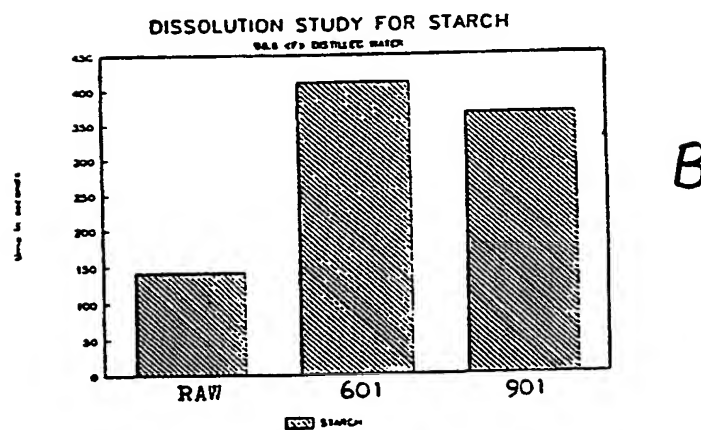
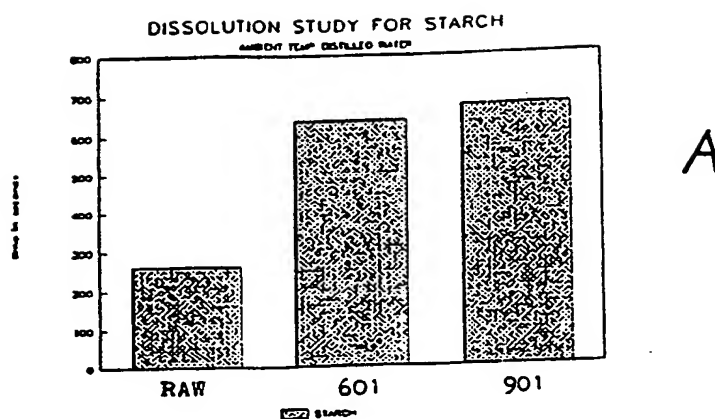
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Operator: MSG  
Run Date: 9-Mar-93 09:20

DSC



10/19

FIG. 6

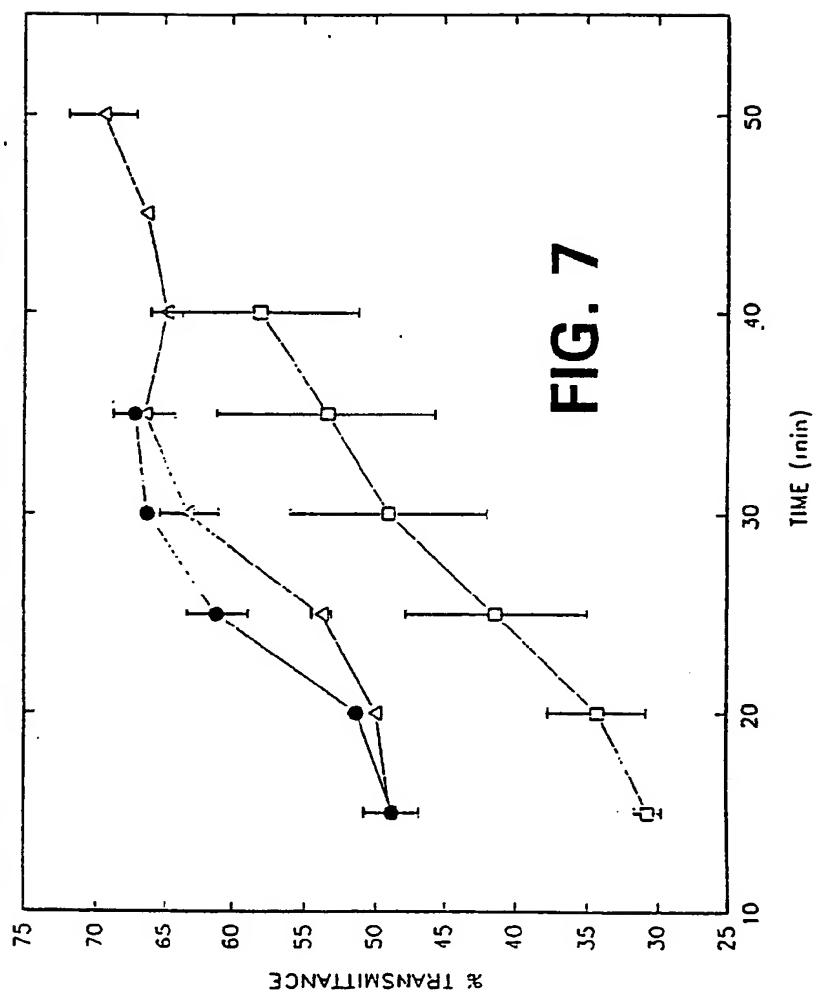


11/19

CHANGE IN TURBIDITY OF 1.0 % (w/w) STARCH DISPERSIONS WITH TIME

Recovered Control (  $\square$  ), 60 PSI (  $\Delta$  ), 90 PSI (  $\bullet$  ).

Disperse at room temperature, measure at 600 nm, Recovered control n=3, full bar=2SD; others n=2, full bar=range

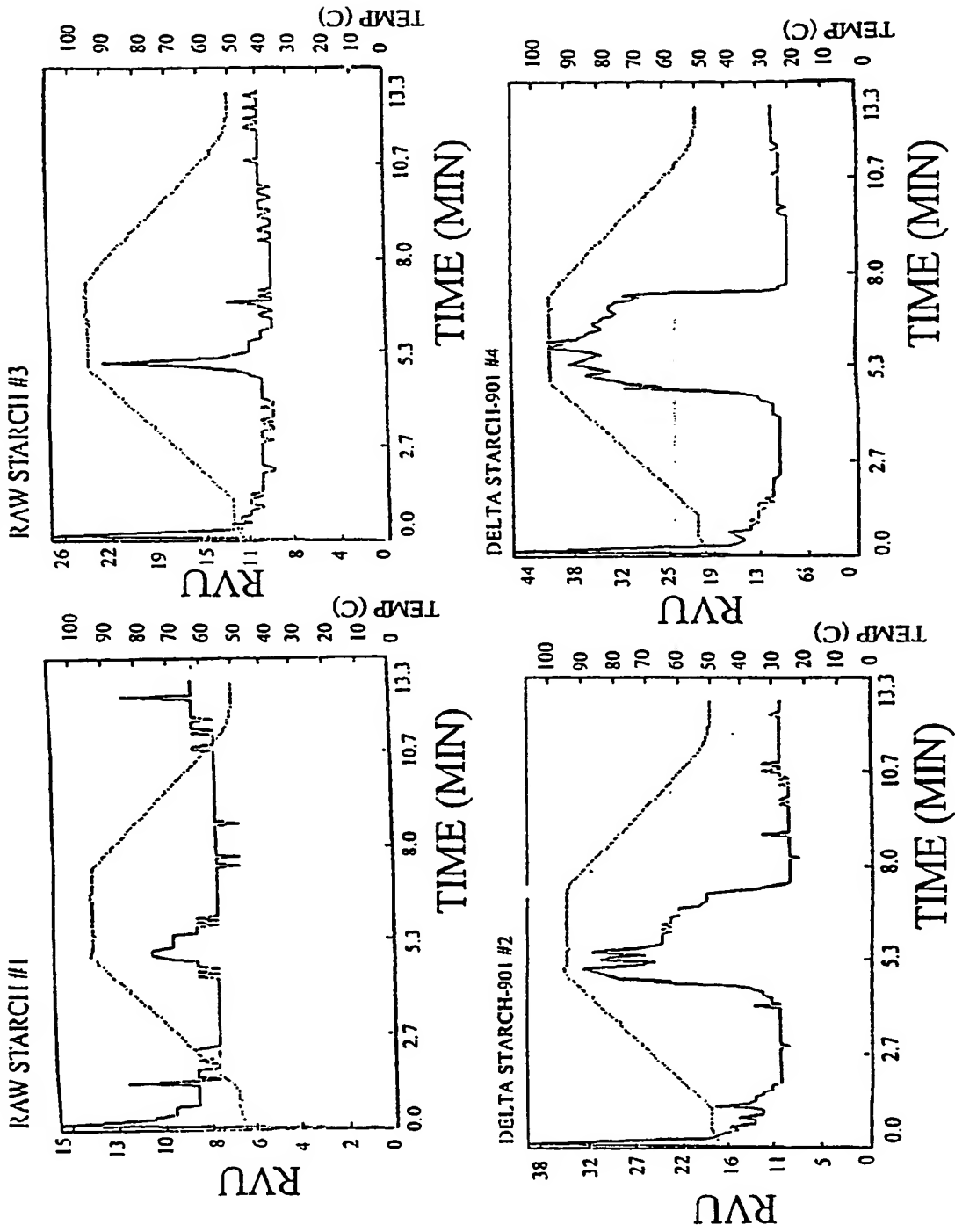


12/19

FIG. 8

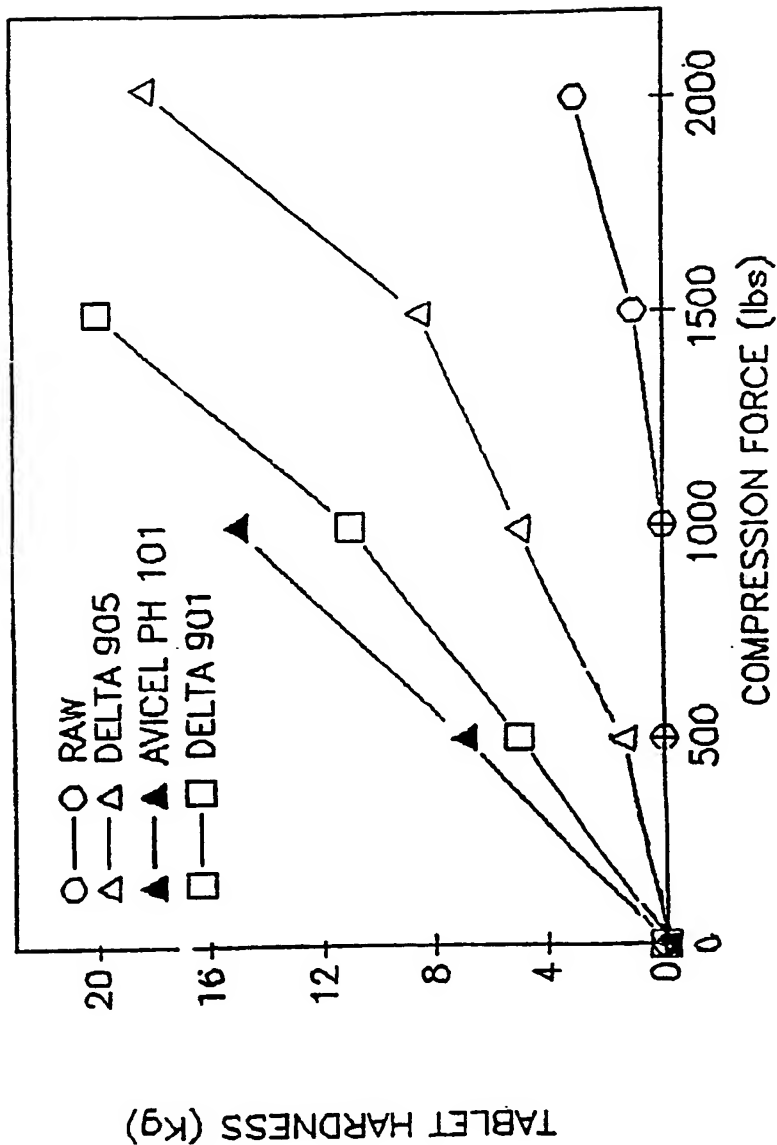
# VISCOSITY

GRAPH 5



GRAPH 6  
HARDNESS vs. COMPRESSION FORCE PROFILE  
OF VARIOUS STARCHES AND MICROCRYSTALLINE CELLULOSE

FIG. 9



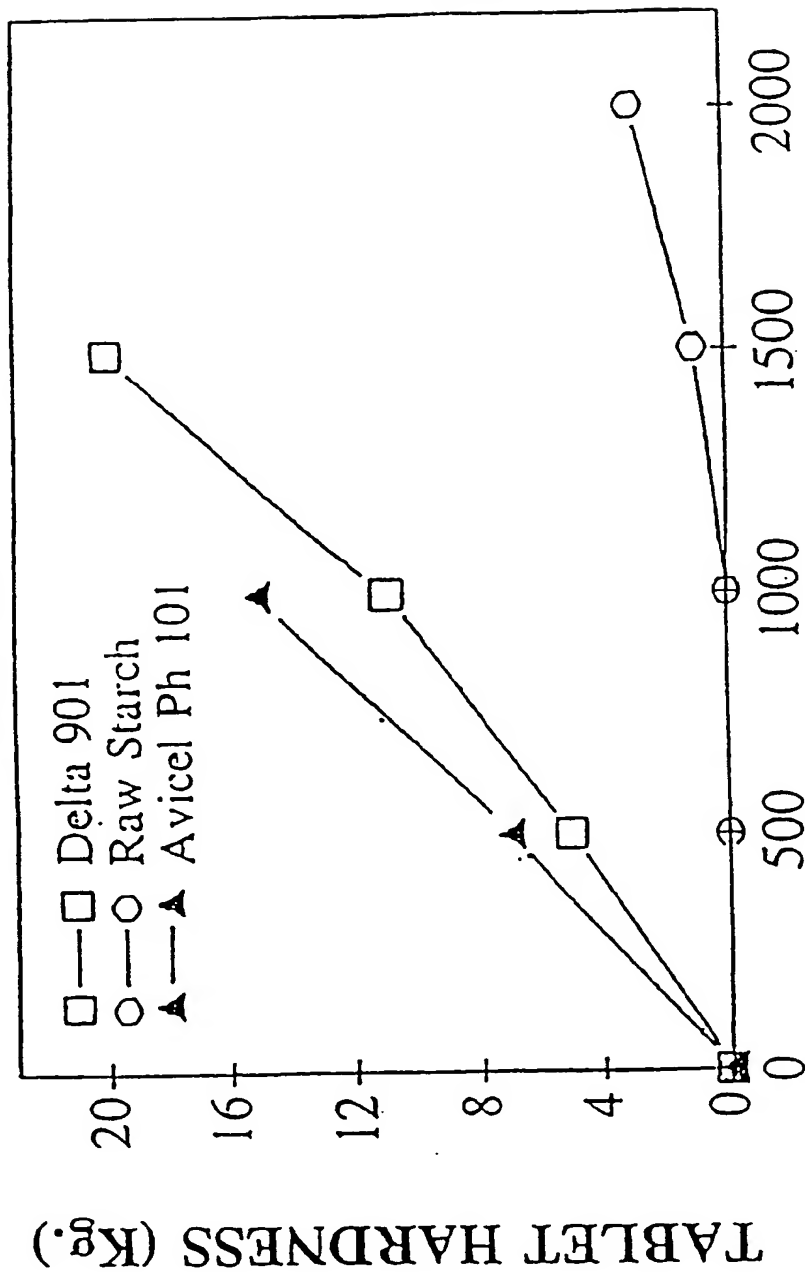
3/8" F.F. TOOLING  
200 mg TABLET WEIGHT

D:ESI1:F:ESI-006

14/19

# HARDNESS PROFILE

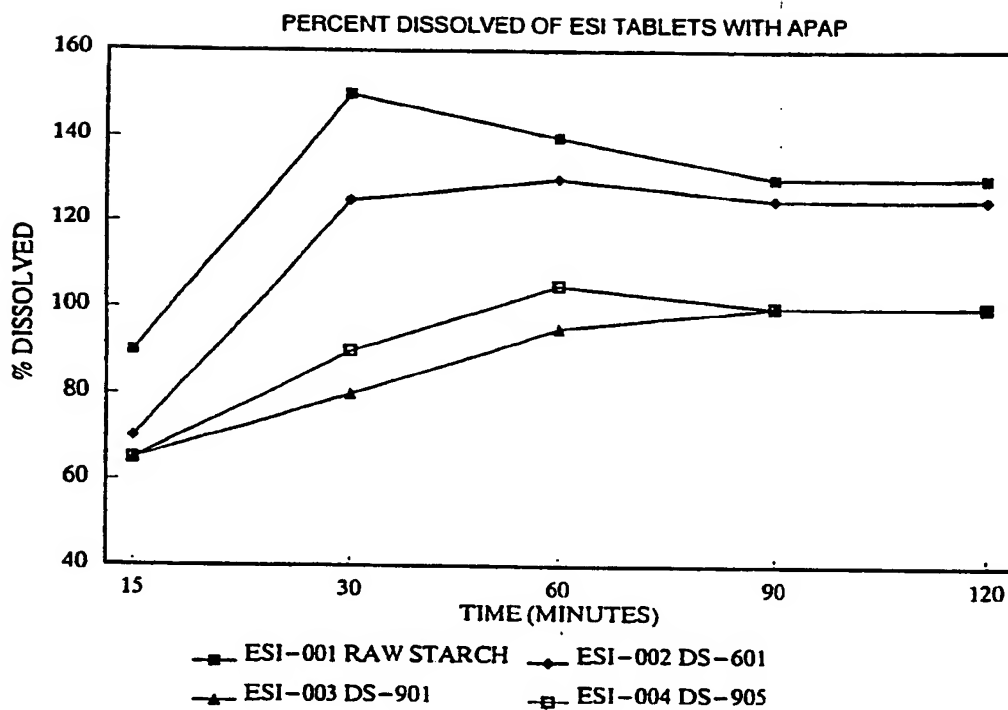
**FIG. 9**



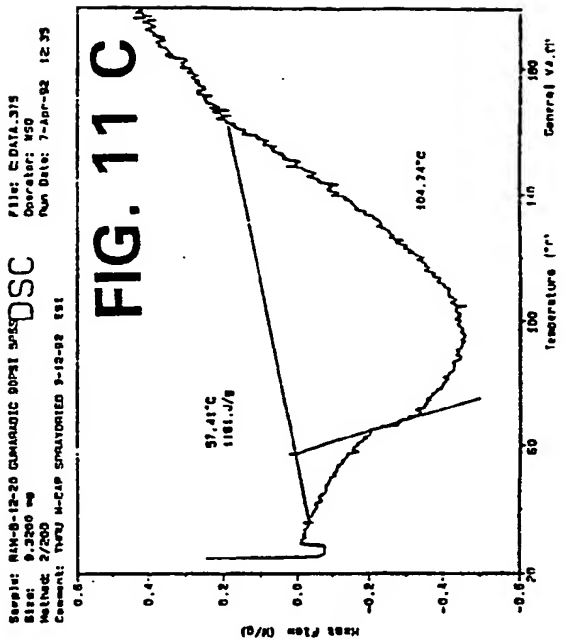
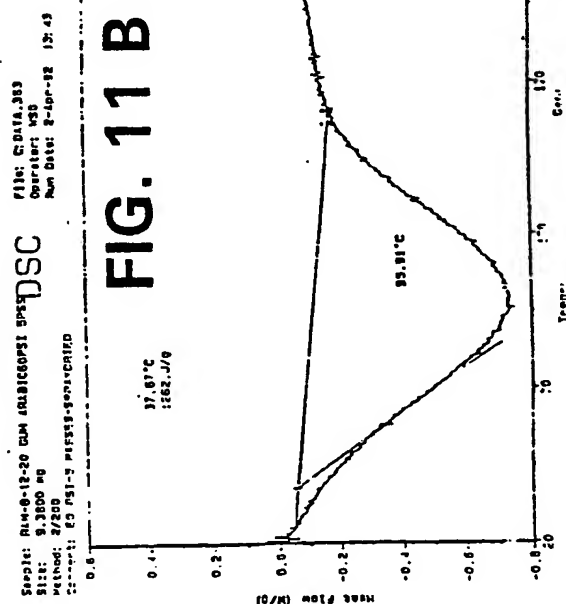
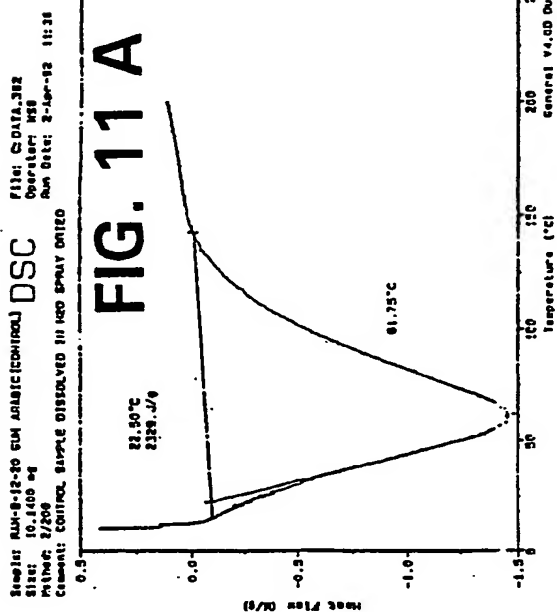
3/8" F.F. Tooling  
200 mg. Tablet Weight

COMPRESSION FORCE (lbs.)

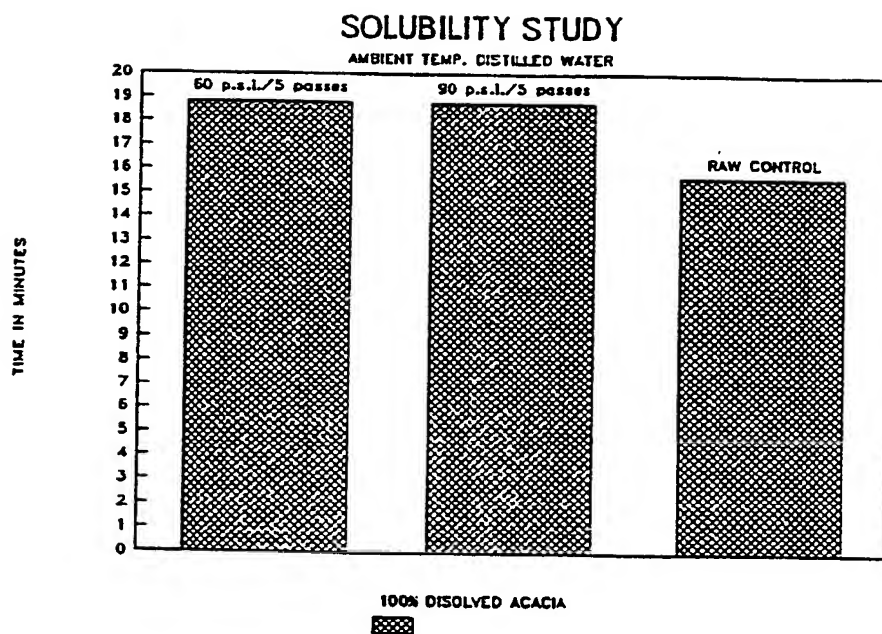
FIG. 10

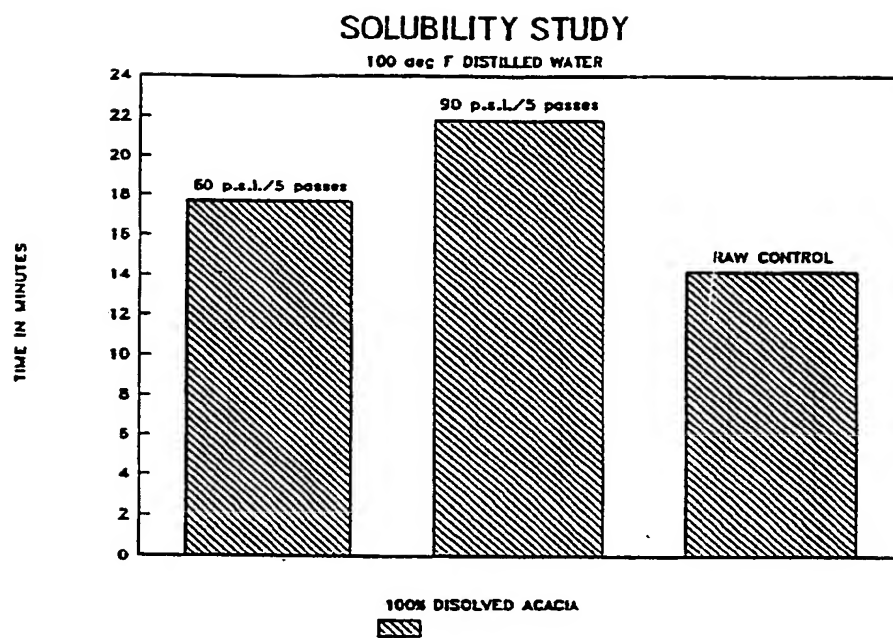


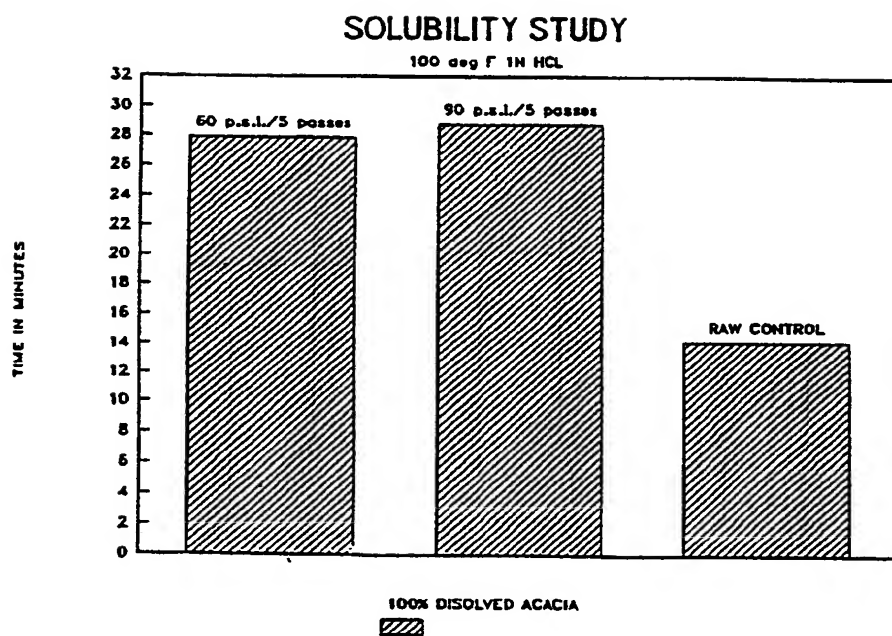




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**FIG. 12**

**FIG. 13**

**FIG. 14**

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/03739

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : Please See Extra Sheet.

US CL : 264/178R

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 425/97; 264/DIG 50, 178R; 72/60

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,449,904 Austen 22 May 1984, (see entire document).	1-13
A,P	US, A, 4,363,611 Austen 14 December 1992, (see entire document).	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	Z	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 JULY 1993

Date of mailing of the international search report

26 AUG 1993

Name and mailing address of the ISA/US  
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/03739

A. CLASSIFICATION OF SUBJECT MATTER:  
IPC (5):

B30B 11/26